

UNIVERSITY OF TORONTO



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INORGANIC CHEMISTRY

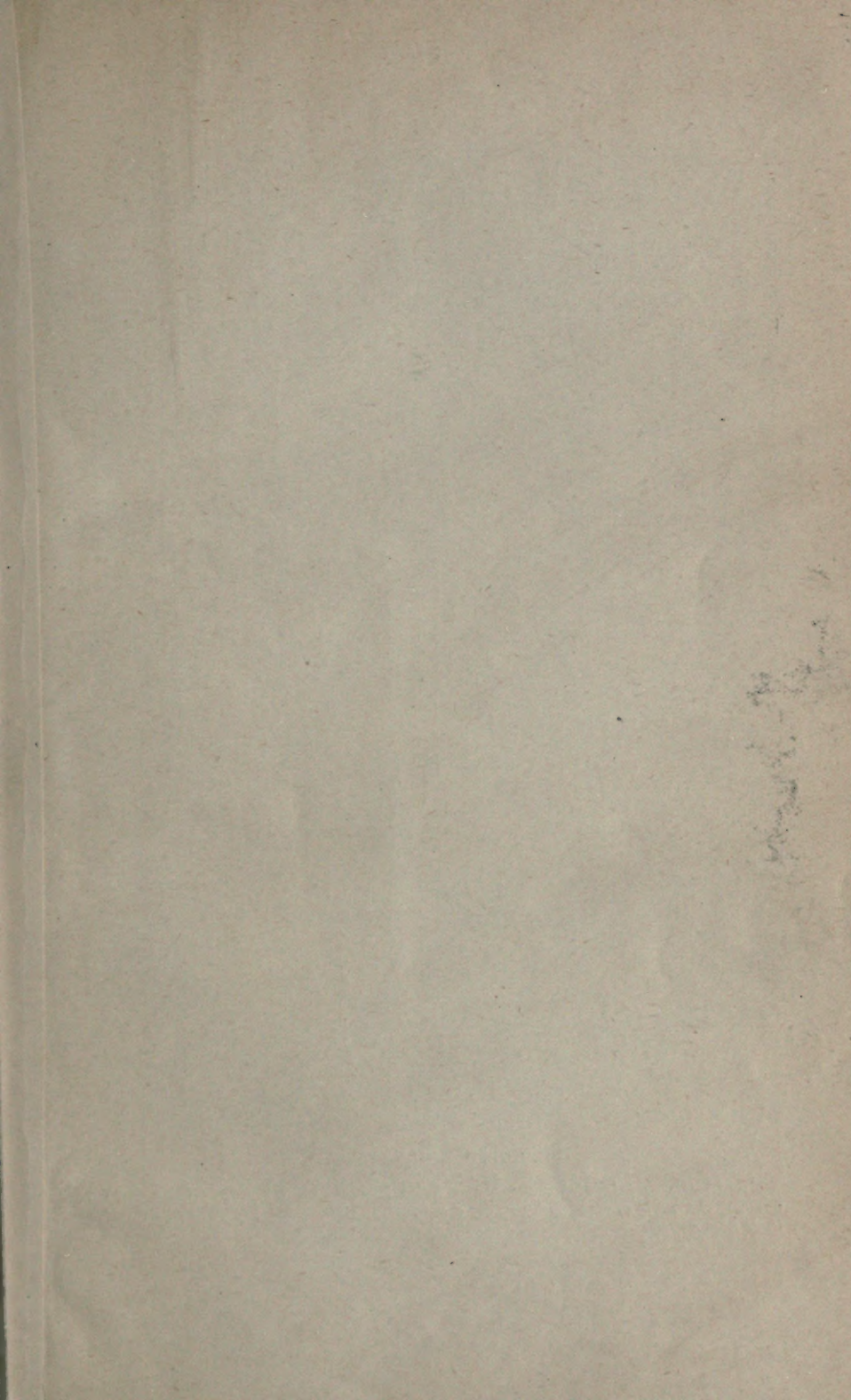
LABORATORY SUPPLIES

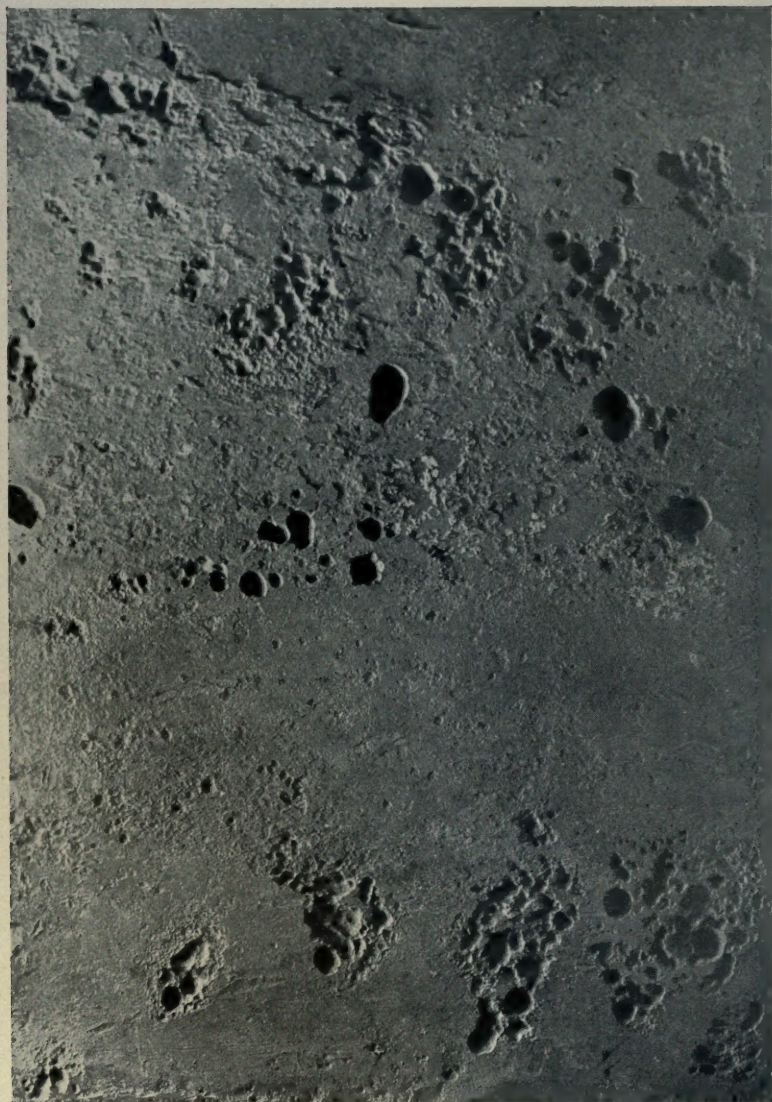
J. A. PALL

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BOILER CHEMISTRY
AND
FEED WATER SUPPLIES





CORRODED BOILER PLATE

NOTE.—In certain lights the crater holes appear as protuberances, but by varying the angle of light or by using a magnifying glass, the pit-holes appear in their true aspect.

BOILER CHEMISTRY
AND
FEED WATER SUPPLIES

BY
J. H. PAUL, B.Sc., F.I.C.
CONSULTING AND ANALYTICAL CHEMIST

WITH FRONTISPIECE

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PREFACE

BOILER Chemistry has not received the attention it merits. A more or less perfunctory analysis of the feed water, made with a view of dealing with the scale-forming constituents, is all that has hitherto been generally considered necessary for boiler work. Little or no investigation has been made, of the innumerable reactions that take place when natural waters are heated to some 400° F. under a pressure of fifteen to twenty atmospheres. Under these conditions new combinations are brought about and unthought-of reactions take place. A modern boiler is not merely a basin in which liquid water is converted into gas, but a receptacle for the mineral impurities contained, in greater or less quantities, in all natural waters even when softened. The boiler is in reality an autoclave in which chemical solutions are concentrated and partially evaporated at high temperatures and pressures, and should be looked upon as a chemical factory in which various chemicals are produced during the conversion of ordinary water from an initial temperature of, say, 60° F. into steam often highly superheated. Some of these reactions affect the steaming capacity of the boiler and others affect the metal of which it is constructed. If these reactions are not properly understood and properly controlled much damage may be done to the metal itself, even if that damage be not sufficient to cause explosion or render the boiler useless for steam-raising purposes. In the following pages a brief account is given of some of these reactions, and attention is called to the conspicuous part played by carbonic acid in boiler chemistry.

Chemistry has improved the physical character of industrial iron and steel, and rendered possible the use of the high pressures now employed in steam boilers, and an acquaintance with the reactions which take place in a boiler under modern working conditions will enable steam users to preserve their boilers from

those evils which are roughly summed up in the expression "scale and corrosion."

Although the internal combustion engine may have a much extended future it does not at present compete with steam in large power plants. The steam boiler up to now is by no means a diminishing quantity, and any chemical knowledge which will increase its efficiency, preserve its life, and save coal deserves thought and consideration.

Coal in the future is most likely to be valued for its chemical products now destroyed in the furnace. Coal will have to be economized, and one way out of the difficulty will be to remove its valuable volatile products by distillation and use the residual cokes for steam-raising purposes. This may present difficulties at first, but these difficulties are not insuperable, and the same skill which has brought the furnace to its present state of perfection will be able to adapt it to the altered conditions.

If it be more beneficial to the human race to utilize benzole for the manufacture of dyes and drugs than to burn it for raising steam, then the valuable benzole will be removed and the carbonaceous residues become the fuel of the future.

Many of the chemical reactions herein described have been gathered from a long practical experience with high-pressure boilers working under varied circumstances and conditions, and the analyses given in the text are original analyses made in the course of a somewhat extended practice.

So far as possible, technical language and expressions have been avoided. The facts stated and the conclusions drawn have been described in the language of everyday life, so that those without more than a very limited acquaintance with chemistry may be able to understand and appreciate the results, and a chapter has been added explaining and illustrating such technical expressions as it has been found necessary to use.

Instead of quoting authorities the principle has here been adopted of giving the evidence itself for statements not generally recognized as common knowledge. It has been felt that the principle of giving authorities is a subterfuge for passing on to others a responsibility an author has not the courage to assume on his own account. This method may not be acceptable to the few, but to the majority it may prove more convenient and satisfactory than the method of referring to some authority in an obscure publication, of which the majority of readers have

never heard, and have neither the means nor time to consult. That part of the work dealing with the action of carbonic acid on iron is largely theoretical and may have to be modified as a more intimate knowledge of this subject is obtained; but where the conclusions drawn from the investigations have been put into practice on a large scale, they have been the means of arresting and preventing much corrosion in boilers and economizers.

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ILLUSTRATION

CORRODED BOILER PLATE . . . { *Frontispiece, and*
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BOILER CHEMISTRY

CHAPTER I

EARTH, AIR AND WATER

WATER is a substance which has the property of assuming different physical forms at different temperatures and pressures. At and below 32° F. it exists in the solid form, at and above 212° F. at ordinary atmospheric pressure it exists as a gas. In the liquid form it is practically incompressible, but as a gas it is compressible, and after it has absorbed the heat necessary to cause it to change its physical state from the liquid form to the gaseous form, any further addition of heat can be transmitted as energy by utilizing its expansive force. Wherever civilization exists water is present, and is therefore the most convenient vehicle for the conversion of heat energy into mechanical energy, and hence its use in boilers.

Chemically speaking, water may be considered a universal solvent, that is to say, it dissolves more or less of any material with which it comes into contact.

The surface of the earth is a more or less solid mass of rocks or strata composed of various combinations of the principal elements, only a few of which exist to any great extent. These rock masses were originally igneous in their origin, and have been formed by the earth gradually cooling down from a mass of incandescent gas. As this cooling took place the less fusible combination of the elements would solidify first, and this partly solid crust would be surrounded by an atmosphere of the less condensible materials. This atmosphere would consist of gases and comparatively volatile material such as chloride of sodium. At this temperature water could not exist, for the heat would be so great that the hydrogen and oxygen would remain apart as gases. As time went on and the earth gradually got cooler the chlorides of the alkalies would condense to form a pellicle

on the surface, and leave nothing but gases, as we know them, to form the atmosphere. By further effluxion of time the cooling process would proceed until a temperature was reached at which the oxygen and hydrogen would combine with explosive violence to form steam. These violent storms, which have been observed in the planet Jupiter, would continue for ages till at last the steam by further loss of heat would condense to water, and this water falling on to the earth's crust would dissolve the pellicle of previously formed chloride of sodium, and the first liquid water on the earth would be a fairly strong solution of chloride of sodium. This solution would form the primeval oceans in the deepest declivities of the earth's surface. Pure water would be evaporated at the hottest parts and condense again in the cooler parts, would wear away the Plutonic rocks and cause fresh levels and contours, and these again in their turn would be altered by the crumpling forces of the gradually cooling crust. Adjustment would take place from time to time until present conditions were arrived at, and the water of the ocean became a 3 per cent. solution of common salt, contaminated with some of the more soluble materials of the earth's skin.

The means by which these transformations have been brought about is a weak solution of oxygen and carbonic acid in water. This is Nature's great destructive agent, which removes mountain masses, dissolving some portions of them, but spreading most of them as an insoluble sediment on the ocean floor. And as all waters in industrial use are waters which are carrying out this destructive process, it is only reasonable to suppose that these waters will be found to contain all sorts and conditions of materials, and that there is no such thing as pure water in Nature.

The atmosphere must be considered to be the worm of a vast still. The water evaporated from the equator is carried up into the higher regions of the atmosphere, and by means of the currents caused by the earth's rotation it is carried away to the temperate regions to be again deposited as rain, or to the arctic or antarctic regions or to high mountains to be deposited as snow or ice.

In passing through the atmosphere rain-water dissolves oxygen and carbonic acid, and finally reaches the earth containing seldom more than 15 c.c., or rather less than 1 cubic inch, of carbonic acid and 30 c.c. of free oxygen per gallon, yet it is this solution which disintegrates the silicates and carries away the chalks.

The chalk is carried away entirely in solution in the form of

bicarbonate of lime, and as it is in a state of true solution the chalk can be and is transported to wherever the water can find its way, and it has been calculated that 275 tons of chalk can be carried away per annum from every square mile of surface. The loss with the igneous rocks is considerably less, but even with these rocks 100 tons per annum of material are continually being carried away in solution from each square mile of the earth's surface. Besides the materials in solution, which comprise the carbonates of lime and the alkalies, the igneous rocks yield a large quantity of impalpable mud or silt. This mud, which is especially prevalent in the waters of tropical rivers, does not easily settle and is often carried many hundreds of miles before it settles and leaves the water clear. This can be seen at the mouths of such rivers as the Amazon, River Plate, Mississippi. The brown muddy water brought down by these rivers can be traced for hundreds of miles before it parts with all its sediment, and it is because the weathering action of the rain-water converts the aluminium silicates into semicolloidal bodies, that the detritus so formed can be carried so far from its place of origin, and be deposited in a position to form new lands and continents. This semicolloidal mud is often a great nuisance where waters have to be used in steam boilers. If it is not removed before entering the boilers, it accumulates in the boiler waters and is often carried up with the rush of steam and finds its way into the steam pipes and engines. As this mud cannot be removed by mechanical filtration, coagulents have to be used, and these are often almost as great a nuisance as the mud. Settlement in large tanks is sometimes effectual, but the tanks have to be so large and the time of settlement so long that this is not always practical. In India some of these tanks are hundreds of yards long and the flow of the water is almost imperceptible, and is further regulated by baffles round which the water must pass before it emerges from the last compartment in a clear state.

The process by which the rocks are disintegrated and separated into soluble and insoluble portions is known as weathering. It is partly a physical and partly a chemical operation, and is brought about by water charged with carbonic acid and free oxygen, aided and assisted by changes of temperature and the scouring action of running water. The first process is in most cases an absorption of water, a kind of hydrolysis whereby the rock mass becomes hydrated, increases in bulk, and is rendered

less resistant to the solvent action of water charged with carbonic acid. Granite may be taken as a typical example of an unweathered rock, and Kaolin of the residual clay to which it is ultimately reduced by the process of weathering.

Granite

Silica	69.33
Alumina	14.33
Ferrous Oxide	3.60
Calcium Oxide	3.21
Magnesium Oxide	2.44
Sodium Oxide	2.70
Potassium Oxide	2.67
Undetermined	1.72
	<hr/>
	100.00
	<hr/>

Kaolin

Silica	48.73
Alumina	37.02
Ferric Oxide79
Calcium Oxide16
Magnesium Oxide11
Sodium Oxide54
Potassium Oxide41
Water of Hydration, etc.	12.24
	<hr/>
	100.00
	<hr/>

A sample of the mud carried down by the River Parana and allowed to settle had the following composition:—

Mud from River Parana

Silica	74.62
Alumina	2.64
Ferric Oxide	5.92
Ferrous Oxide	2.02
Water of Hydration	12.88
Organic Matter, etc.	1.92
	<hr/>
	100.00
	<hr/>

This mud was so difficult to settle that some of it generally found its way into the boilers, and from there, so fine was its state of division that it eventually found its way into the steam pipes and engines. An analysis of the mud collected from the steam traps is given below.

Mud from Steam Traps

Silica	55.80
Alumina	10.65
Ferric Oxide	14.75
Ferrous Oxide86
Carbonate of Lime	3.00
Magnesium Oxide	2.16
Water of Hydration	10.16
Organic Matter, etc.	2.62
	<hr/>
	100.00
	<hr/>

Although silica is only soluble in pure water to the extent of about .25 grains per gallon, in water containing alkaline carbonates it is very much more soluble. As the rock masses undergo weathering, they break up into smaller particles and therefore expose a very much larger surface to the solvent action of the water, and calculations have been made which show that a cubic foot of fine sand or clay exposes as much as 160,000 square feet of surface to the action of the water. Hence once the disintegration of the solid mass is fairly started the solution proceeds with greater rapidity and the water carries away increased quantities of the soluble materials.

In some cases the hydrated silicates of lime and alumina acquire the remarkable property of being able to exchange their bases with the salts in the percolating water. Thus a hydrated silicate of alumina and lime, when exposed to the percolation of a water containing chloride of sodium, gives up its lime and retains in its place an equivalent of soda. The outflowing water therefore contains chloride of calcium instead of sodium chloride, and the weathering rock becomes a silicate of alumina and soda instead of alumina and lime. In this way these zeolites, as they may be described, can often change the character of a water percolating through them. Soft alkaline soda-waters are often found in wells deep down in the chalk, where a hard carbonate of lime-water would naturally be expected, but when such waters are traced to their origin it is generally found that they have come from zeolitic sands or siliceous materials of similar origin. This property of exchanging bases in waters is not confined to the zeolites, as lavas and other rocks of igneous origin possess the property when they become partially hydrated. The principal soluble impurities carried by water from the land to the sea are silica, carbonate of lime, sulphate of lime, carbonate of soda, carbonate of potash and chloride of sodium.

The carbonate of lime is largely removed from sea-water by the activity of minute animalculæ such as the Foraminifera and the Coral insect. The latter form vast reefs of carbonate of lime, and the former spread a sludge of carbonate of lime on the ocean floor. The function of the sponges is to remove the silica, and the seaweeds, which are abundant on nearly every coast all over the world, probably remove much of the sulphates, as their ashes are highly charged with the sulphates of potash and soda.

With the exception of the chloride of sodium, the soluble impurities carried into the sea are removed by these agencies. As to the chloride of sodium there is some evidence to show that this may be very slowly accumulating.

It is therefore evident that any sample of natural water is bound to contain, in addition to its gaseous contents, more or less mineral matters, the quality and quantity of which will depend upon the geological nature of the district through which it flows, and a very good idea of the geological nature of a district can often be gathered from an analysis of the waters obtained from it.

NATURAL WATERS

The quantity of material dissolved in these natural waters is generally small when compared with the volume of the water. Thus if we take a sample of the London waters and make a percentage analysis of it, the figures would come out as follows :—

Silica	·0003
Oxide of Iron	·0002
Sulphate of Lime	·0091
Carbonate of Lime	·0177
Nitrate of Lime	·0008
Sulphate of Magnesia	·0022
Nitrate of Sodium	·0034
Chloride of Sodium	·0047
Water	99·9616
	<hr/>
	100·0000
	<hr/> <hr/>

Such an analysis would convey the impression that the water was practically pure, as any commercial article which contained 99·96 per cent. of its principal constituent would certainly be regarded as pure. But in this case the water is rather a bad one and contains what is called 18·7° of Hardness, though the analysis only shows a total impurity of ·0384 per cent., and it is more convenient, and gives a better idea if the analysis is recorded in

another form, as the percentage composition lands some of the constituents in the fourth place of decimals. This can be overcome by recording the figures in parts per 100,000, and the analysis would read thus:—

Silica	·30
Oxide of Iron	·20
Sulphate of Lime	9·10
Carbonate of Lime	17·70
Nitrate of Lime	·80
Sulphate of Magnesia	2·20
Nitrate of Sodium	3·40
Chloride of Sodium	4·70
Water	99,961·60
	<hr/>
	100,000·00
	<hr/>

Water analyses are often recorded in this way, leaving out the water, adding up the other constituents and calling them the total solids in the water.

As the gallon in this country is taken as the unit of measure, it is found more convenient to record the results in parts per gallon. A gallon contains 70,000 grains, and the result in grains per gallon can easily be obtained by multiplying the figures in the last analysis by ·7, thus:—

	Grains per Gallon.
Silica	·21
Oxide of Iron	·14
Sulphate of Lime	6·37
Carbonate of Lime	12·39
Nitrate of Lime	·56
Sulphate of Magnesia	1·54
Nitrate of Sodium	2·38
Chloride of Sodium	3·27
	<hr/>
	26·86
	<hr/>

The water is left out, the result is given in grains per gallon and the total solids shown. It is in this form that the water analyses in this work are recorded. For industrial purposes this is the most convenient form, as it readily affords the data for calculating the amount of any of these materials in the Engineer's unit of water, that is per 1000 gallons. One gallon of water weighs 10 lb. and 1000 gallons 10,000 lb., so that by multiplying any of these figures by 1000, the number of grains in 10,000 lb. is obtained. But as 1 lb. = 7000 grains, therefore by multiplying the number of grains by 1000 and dividing by 7000, the number of lbs. per 1000 gallons is obtained. And as

$\frac{1000}{7000} = \frac{1}{7}$ so by dividing any of the figures in an analysis (in grains per gallon) by 7 the number of lbs. of that substance in 1000 gallons of the water is at once obtained. In the above analysis the amount of carbonate of lime per 1000 gallons of water is $\frac{12.39}{7} = 1.77$ lb., and the total solids $\frac{26.86}{7} = 3.84$ lb. In this way from an analysis it is an easy matter to calculate the amounts of scale-forming materials in any water. In the case of the water under discussion, the scale-forming materials are sulphate of lime 6.37 grains and carbonate of lime 12.39 grains, the amount of scale-forming material is therefore $\frac{6.37 + 12.39}{7} = \frac{18.76}{7} = 2.7$ lb. per 1000 gallons nearly.

If the boiler evaporates 20,000 gallons of this water per day, the amount of scale-forming materials deposited will be $20 \times 2.7 = 54$ lb. daily.

Looking at an analysis in this light, a very simple calculation will give a very good idea of the amount of scale that can be formed in a boiler. It has this further advantage, that the amount of the soluble salts remaining in the boiler water can also be calculated and an idea of the concentration readily formed. In this case the soluble salts are, nitrate of lime .56, sulphate of magnesia 1.54, nitrate of sodium 2.38, and chloride of sodium 3.29, total 7.77 grains per gallon, and $\frac{7.77}{7} = 1.11$ lb. per 1000 gallons, and if the evaporation has been 100,000 gallons, the amount of total soluble salts put into the boiler has been $1.11 \times 100 = 111$ lb.

We have thus a record of quantities in a definite weight or volume of water, not a mere expression of parts in an empirical volume. Where the evaporative capacity of a boiler is calculated in lbs. of water, the grains per lb. are at once obtained by moving the decimal point one place to the left.

If the results are recorded in parts per 100,000 a calculation has to be made every time the result is required in gallons of water to be softened or treated or in lbs. of water to be evaporated.

So much having been said for the method of recording the analysis, some description can now be given of the various kinds of natural waters.

The atmosphere, especially in industrial and thickly populated districts, always contains a certain amount of dust. This dust

contains much soluble matter, as will be seen from the following analysis :—

Atmospheric Dust

Silica	49·01
Oxide of Iron	6·84
Sulphate of Lime	12·34
Carbonate of Lime	10·25
Sulphate of Magnesia	1·77
Chloride of Ammonium	·05
Chloride of Sodium	·53
Organic Matter	14·63
Moisture	4·55
	<hr/>
	99·97
	<hr/>

Some of this dust was shaken up with distilled water and the water on analysis was found to contain :—

Dust-water

	Grains per Gallon.
Silica	·04
Oxide of Iron	·05
Sulphate of Lime	3·76
Carbonate of Lime	·23
Sulphate of Magnesia	·15
Chloride of Ammonia	·06
Chloride of Sodium	·18
Organic Matter	·63
	<hr/>
	5·10
	<hr/>

By comparing this analysis with some of the analyses of rain-water given further on, it will be seen that this water is exactly like a rain-water.

Soot, which is freely poured into the atmosphere in large towns and inhabited districts, also contains much soluble matter.

Soot

Silica	5·42
Oxide of Iron	8·64
Sulphate of Lime	2·58
Carbonate of Lime	1·76
Sulphate of Magnesia	·60
Chloride of Ammonia	21·93
Humus Matter	8·85
Oily Matter	4·30
Moisture	1·06
Carbon (diff.)	44·86
	<hr/>
	100·00
	<hr/>

The water obtained by digesting this soot in distilled water contained:—

Soot-water

	Grains per Gallon.
Silica	·01
Oxide of Iron	·01
Sulphate of Lime	4·43
Sulphate of Magnesia	·09
Sulphate of Ammonia	5·41
Carbonate of Ammonia	·94
Chloride of Ammonia	26·78
Ammonia combined with Humus matters	8·25
	<hr/>
	45·92
	<hr/>

This is a much stronger solution than ordinary rain-water, but it could easily have been made more dilute to make it comparable with rain-water.

Some of this soot-water was left in contact with chalk for three months and then analyzed and found to contain the following:—

Soot-water in Chalk

	Grains per Gallon.
Silica	·03
Oxide of Iron	·17
Sulphate of Lime	10·70
Carbonate of Lime	6·43
Sulphate of Magnesia	·19
Chloride of Ammonia	23·34
Nitrate of Ammonia	3·47
	<hr/>
	44·33
	<hr/>

The chalk itself contained:—

Chalk

Carbonate of Lime	98·64
Carbonate of Magnesia	·48
Silica	·81
	<hr/>
	99·93
	<hr/>

The action of the chalk is to convert the sulphate of ammonia into sulphate of lime, and also to convert a portion of the ammonia into nitrate. Three months is not a long time to leave the water in contact with the chalk. Many natural waters drawn from the chalk may have been there thousands of years. This water was only left in contact, not slowly percolated through

chalk. Had it been slowly percolated for a long period it is highly probable that all the ammonia would have been converted into nitrate. It is therefore possible that the nitrate of lime so frequently found in chalk-waters is formed in this way, that is, by conversion of atmospheric ammonia, rather than from sewage ammonia. Some of the nitrate is no doubt derived from the atmosphere itself, but none of the rain-waters of which the analyses are here given contained any appreciable quantity of nitric acid although they contain considerable quantities of ammonia.

The foregoing experiments were made with soot from a domestic chimney and which therefore contained a large quantity of ammonia. Soot from a chimney under which the fuel is burnt under considerable draught does not contain ammonia, as the ammonia is destroyed by the extra heat in the presence of excess of air. The following analysis shows the composition of soot from a furnace chimney.

Furnace Soot

Silica	14.52
Ferric Oxide	14.13
Ferrous Oxide	1.72
Sulphate of Lime	7.87
Sulphate of Magnesia	2.01
Sulphate of Soda	2.27
Chloride of Sodium	5.06
Moisture	1.50
Carbon (diff.)	50.92
	<hr/>
	100.00
	<hr/>

The water derived from this would contain no ammonia, but would contain some sulphate of soda and sulphate of lime.

In addition to the solid impurities present in the atmosphere gaseous impurities are being continually added to it. These gases are principally carbon dioxide and sulphur dioxide. For the purpose of illustration coal may be taken as containing 80 per cent. Carbon and 1 per cent. of Sulphur. This means that the combustion of every ton of coal puts into the atmosphere 2.93 tons of carbon dioxide and 67 lb. of sulphuric acid, assuming that the whole of the sulphur dioxide is fully oxidized in the air. And in industrial districts where many furnaces are at work the rain-water is distinctly and decidedly acid.

The direction of the wind will determine the flow of this acid into other districts where the atmosphere is not normally acid,

and it is quite possible to have the rain-water in certain districts sometimes acid and sometimes neutral. This will depend upon the direction of the wind. This intermittent acidity often causes much corrosion, before the cause is located.

Acid Rain-water (Yorkshire)

	Grains per Gallon.
Silica01
Oxide of Iron08
Sulphate of Lime	1.73
Sulphate of Magnesia47
Chloride of Ammonia39
Chloride of Sodium78
Sulphuric Acid26
	<hr/>
	3.72
	<hr/>

One of the functions of rain-water in the economy of Nature is to cleanse the atmosphere from the soluble impurities poured into it. The two following analyses show the composition of the rain-water at the beginning and at the end of twenty-four hours' continuous rain in one place.

Rain-water (First Washings of the Air). London, S.W.; Wind W.

Silica01
Oxide of Iron22
Sulphate of Lime	2.24
Sulphate of Magnesia32
Nitrate of Ammonia05
Sulphate of Ammonia73
Carbonate of Ammonia39
Chloride of Ammonia55
Chloride of Sodium56
Organic Matter	1.41
	<hr/>
	6.48
	<hr/>

Rain-water after Twenty-four Hours' Continuous Rain. London, S.W.; Wind W.

Silica01
Oxide of Iron15
Sulphate of Lime99
Carbonate of Lime05
Carbonate of Magnesia12
Nitrate of Ammonia03
Carbonate of Ammonia16
Chloride of Ammonia13
Chloride of Sodium10
	<hr/>
	1.74
	<hr/>

Rain-water after Four Hours' Rain. London, S.W.; Wind S.W.

Silica	·01
Oxide of Iron	·08
Sulphate of Lime	2·54
Carbonate of Lime	1·04
Carbonate of Magnesia	·06
Nitrate of Ammonia	·08
Carbonate of Ammonia	·24
Chloride of Sodium	·81
	<hr/>
	4·86
	<hr/>

Rain-water after Twenty-two Hours' Continuous Rain. Same place; Wind S.W.

Silica	·01
Oxide of Iron	·01
Sulphate of Lime	·29
Carbonate of Lime	·31
Nitrate of Ammonia	·01
Chloride of Ammonia	·36
Chloride of Sodium	·02
	<hr/>
	1·01
	<hr/>

Rain-water. London, E.; Wind W.

Silica	·01
Oxide of Iron	·92
Sulphate of Lime	3·06
Chloride of Calcium	5·89
Chloride of Magnesia	·55
Chloride of Ammonia	3·16
Chloride of Sodium	1·75
	<hr/>
	15·34
	<hr/>

This sample was taken at Barking, and the wind being west, the smoke of London would tend this way, whilst the S.W. districts would be comparatively free from town contamination.

Rain-water in Country (Kent). Wind S.W.

Silica	·08
Sulphate of Lime	·99
Carbonate of Lime	1·65
Carbonate of Magnesia	·33
Carbonate of Ammonia	·09
Chloride of Sodium	1·23
	<hr/>
	4·37
	<hr/>

BOILER CHEMISTRY

Rain-water. Lowestoft; Wind off Sea

Silica	·03
Sulphate of Lime	1·00
Carbonate of Lime	1·54
Chloride of Magnesia	·06
Chloride of Ammonia	·12
Chloride of Sodium	1·46
	<hr/>
	4·21
	<hr/>

Snow. London, S.W.

Silica	·20
Oxide of Iron	·11
Sulphate of Lime	1·29
Sulphate of Magnesia	·31
Sulphate of Sodium	·48
Nitrate of Ammonia	·10
Chloride of Ammonia	·87
Chloride of Sodium	·43
	<hr/>
	3·79
	<hr/>

Hail

Silica	·08
Oxide of Iron	·22
Sulphate of Lime	1·64
Carbonate of Lime	·27
Chloride of Calcium	·29
Chloride of Magnesia	·19
Chloride of Ammonia	·26
	<hr/>
	2·95
	<hr/>

Rain-water (Mid-Ocean)

Silica	·10
Oxide of Iron	·20
Sulphate of Lime	·11
Carbonate of Lime	·72
Sulphate of Magnesia	·36
Chloride of Sodium	2·45
	<hr/>
	3·94
	<hr/>

This sample was collected during a heavy rain-storm at least 1000 miles from land.

Acid Rain-water (Sleet). London, S.E., 1918

Sulphate of Lime	·31
Chloride of Calcium	·91
Sulphate of Sodium	·69
Chloride of Sodium	·65
Organic Matter	·65
Hydrochloric Acid	·51
Ammonia	trace

3·72

Hardness 1·10°

Snow. London, S.E., 1918

Nitrite of Lime	·15
Chloride of Calcium	·88
Sulphate of Sodium	·89
Chloride of Ammonia	·15
Organic Matter	·22
Hydrochloric Acid	·20

2·49

Hardness ·90°

Rain. London, S.E., 1918

Chloride of Calcium	·31
Sulphate of Lime	·68
Chloride of Sodium	·80
Hydrochloric Acid	·31
Ammonia	trace

2·10
Rain. London, S.E., 1918; Wind N.

Silica	·04
Oxide of Iron	·66
Sulphate of Lime	4·57
Chloride of Magnesia	·19
Organic Matter	3·08
Chloride of Ammonia	·30
Hydrochloric Acid	1·02
Nitrites	traces

9·26

Hardness 3·50°

When this was filtered through chalk, the acid was neutralized and the hardness increased to 5·5 grains per gallon.

From these and other analyses it appears that it is only in the neighbourhood of cities and large industrial centres that there is any appreciable quantity of ammonia or acid in rain-water, and that the rain deposited over the sea and the open country contains sulphate and carbonate of lime with more or less chloride of sodium. And as all the samples analyzed contain sulphate of lime, it is probable that this is the origin of the small quantities of sulphate of lime so universally prevalent in natural waters. When the quantity is much in excess of the quantities found in rain-water, then the sulphate of lime is introduced by the percolation of the water through strata containing it.

Rain-water as it reaches the ground is always contaminated with or contains some soluble matters, and these are generally solid matters. The gaseous impurities are carbonic acid about .5 grain per gallon and about 30 c.c. of dissolved oxygen.

The ultimate destination of this rain-water is determined by many factors, such as the incline and character of the ground, its permeability and the rapidity with which the water runs off. Part of it runs off the surface to form streams and rivers, part of it percolates the soil and part is re-evaporated. River-water when not fed by springs usually contains much less soluble matter than spring-waters, which are percolation waters and therefore have had greater opportunity of dissolving matters with which they come in contact.

Well-waters are like spring-waters insomuch as they have percolated certain porous strata before they are held up by impervious strata. It will therefore be evident that the character of the water will be determined by the surfaces over which it has passed and by the character of the strata through which it percolates. Thus rain-water collected from metamorphic or granitic rocks will remain little else than rain-water.

On the other hand, when the water passes through the chalk or Magnesium Limestones it comes into contact with much that it can dissolve, and which it can and does dissolve to a very appreciable extent, so that waters taken from the chalk frequently contain as much as 30-40 grains of carbonate of lime, while waters from magnesium limestones sometimes attain a hardness of 100°. Although rain-water on reaching the ground only contains sufficient free carbonic acid to dissolve 1 grain of carbonate of lime per gallon, nevertheless it is able to obtain sufficient carbonic acid to dissolve large quantities of carbonate

of lime and magnesia, that is, to convert them first into bicarbonate and then to dissolve them as such. This is accounted for by the fact that the chalk or limestone is always covered by a layer of subsoil which furnishes some of this carbonic acid, while fissures and caverns in the rock furnish the remainder. In fact carbonic acid is frequently found in mines and caverns under very considerable pressure, and it is so widely diffused through underground strata, that waters percolating through these strata become highly charged with it. It is these sources of carbonic acid which enable water to dissolve the amount of carbonate of lime usually found in waters taken from carboniferous formations. The amount of carbonate of lime removed from the earth's surface by carbonic acid in water is enormous, and it has been calculated that the average quantity so removed amounts to 50 tons per square mile per annum over the whole earth's surface.

The accompanying diagrams give the daily amount of free and fixed carbonic acid, in grains per gallon, in the Kent Company's Supply during 1904-5.

The samples were taken and tested every day for twelve months, and it will be seen that the free carbonic acid varied between 7-12 grains and that only on very occasional cases did the free carbonic acid ever coincide with the fixed, that is, with the carbonic acid existing as carbonate. The free carbonic acid which is necessary to dissolve the chalk must have come into the water after it reached the ground, and carbonic acid may therefore be considered to be one of the normal products of subterranean action.

Reference to the diagrams will show that the free carbonic acid does not bear any fixed ratio to the combined carbonic acid. This is a fact of considerable importance and will be better appreciated when the process of water softening is dealt with.

FREE AND FIXED CARBONIC ACID IN LONDON WATER, 1904-1905.

The figures are in grains per gallon. The upper curve records the free and the lower curve the fixed carbonic acid.

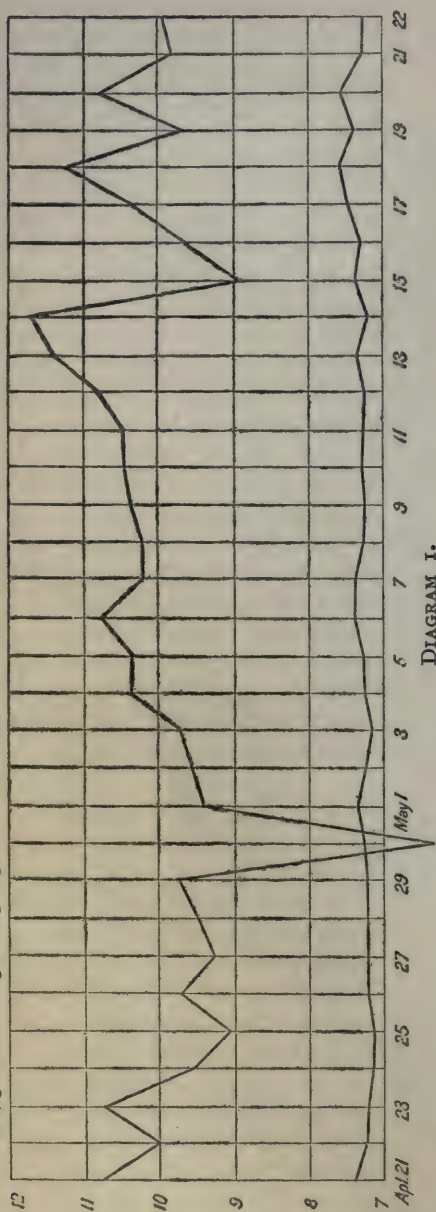
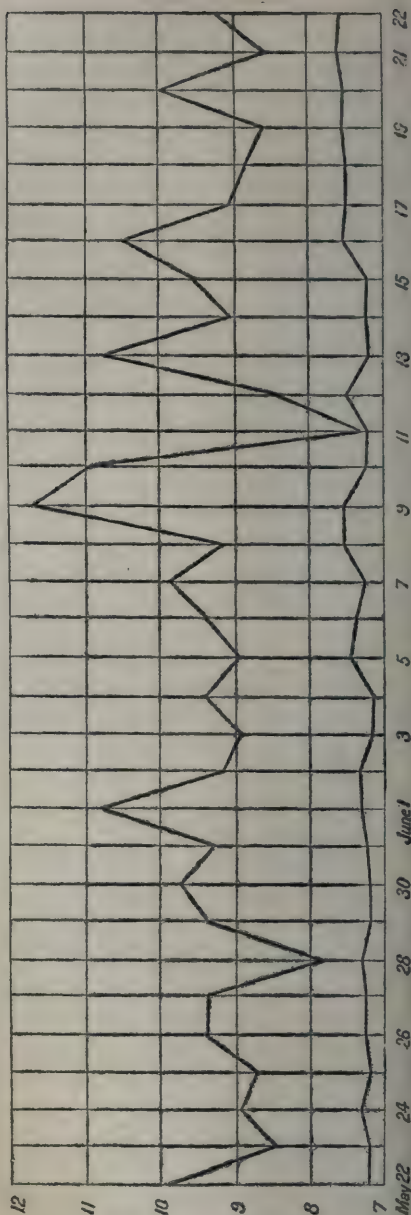


DIAGRAM I.



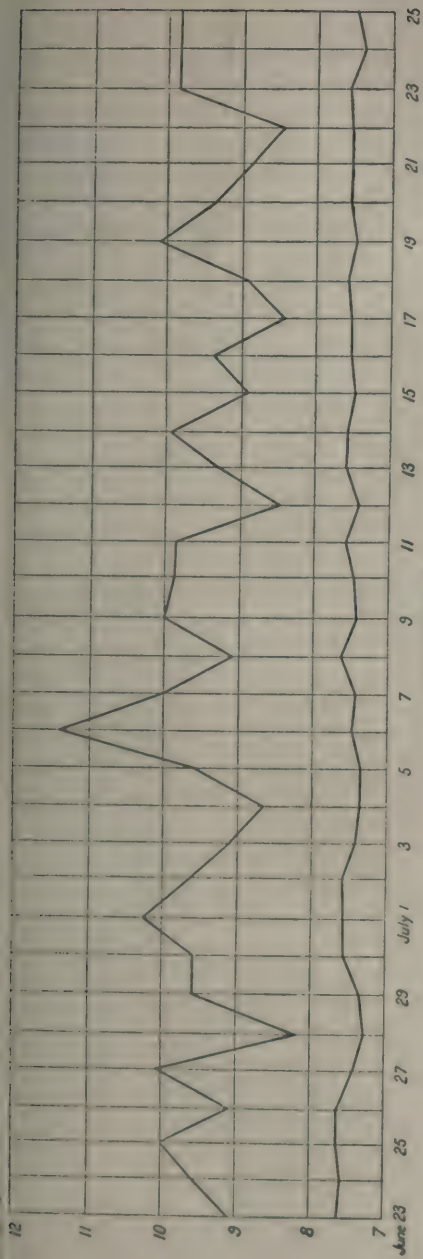


DIAGRAM 3.

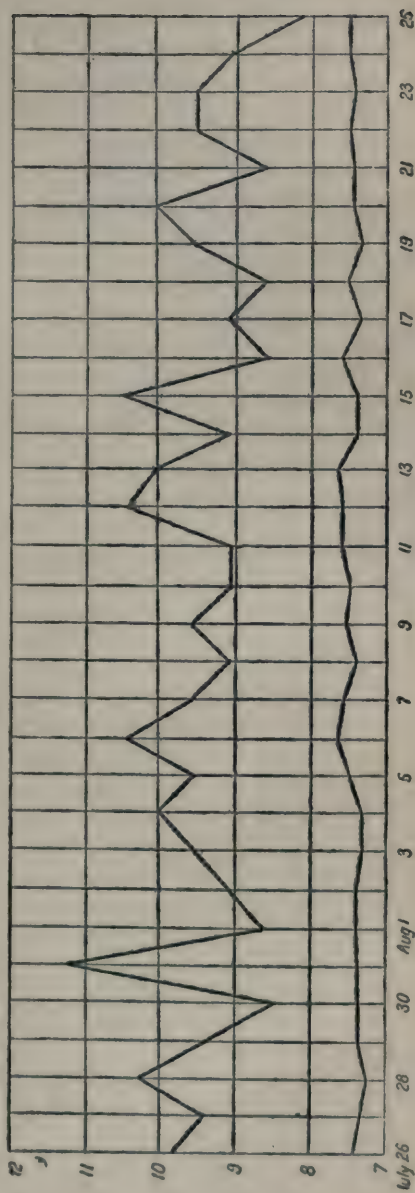


DIAGRAM 4.

FREE AND FIXED CARBONIC ACID IN LONDON WATER, 1904-1905.
The figures are in grains per gallon. The upper curve records the free and the lower curve the fixed carbonic acid.

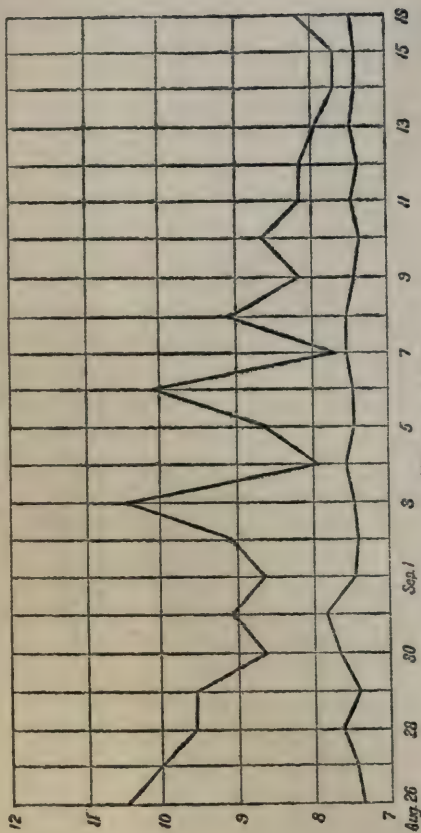
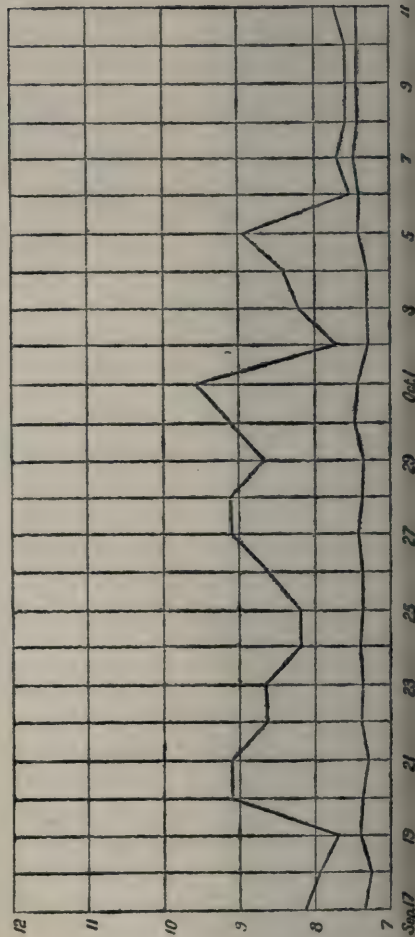


DIAGRAM 5.



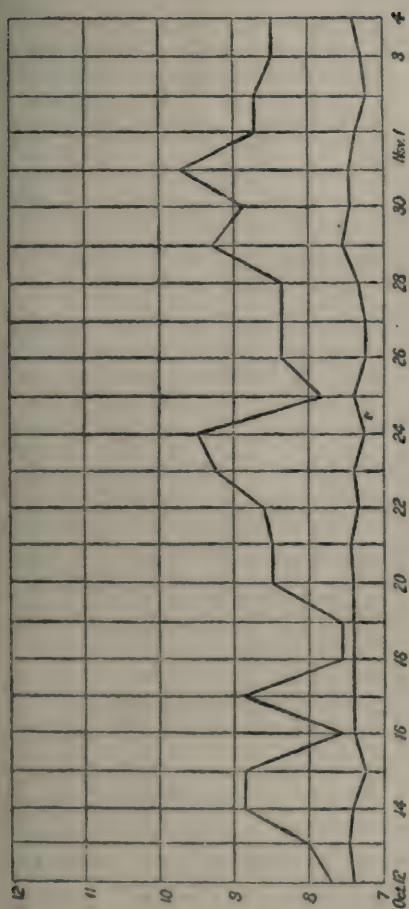


DIAGRAM 7.

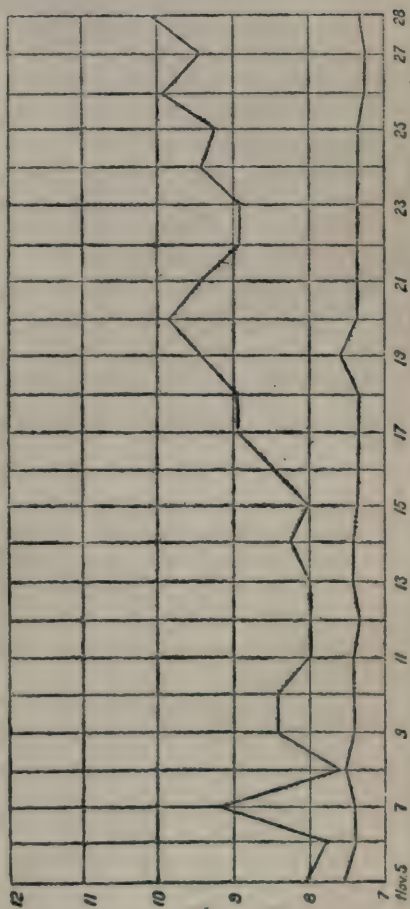


DIAGRAM 8.

FREE AND FIXED CARBONIC ACID IN LONDON WATER, 1904-1905.
The figures are in grains per gallon. The upper curve records the free and the lower curve the fixed carbonic acid.

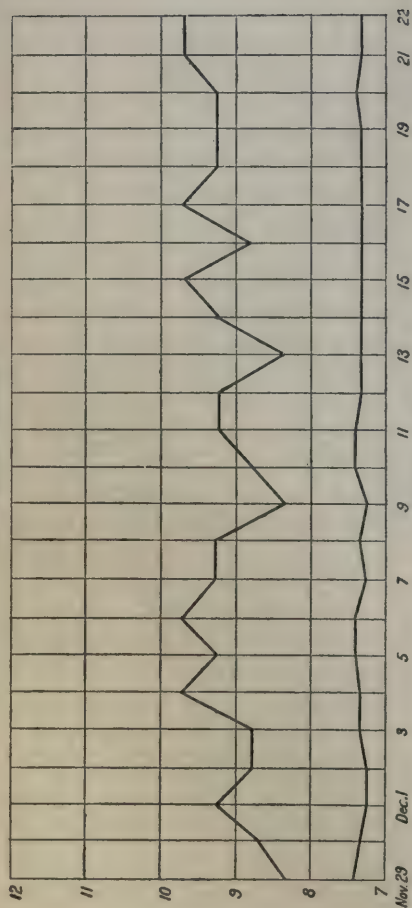
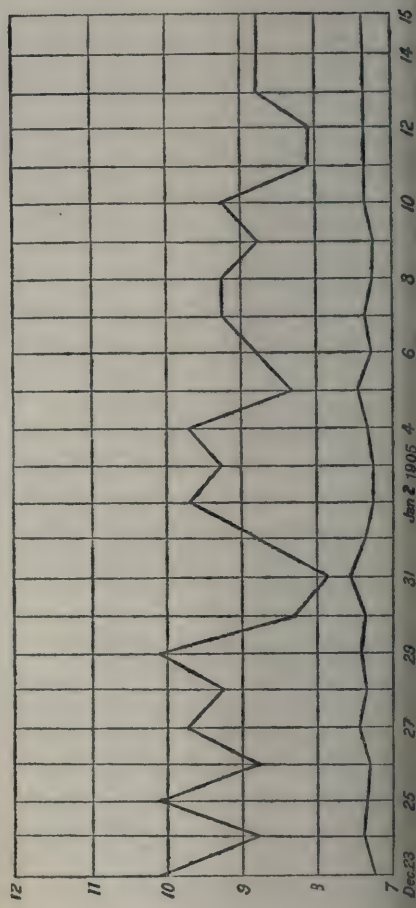


DIAGRAM 9.



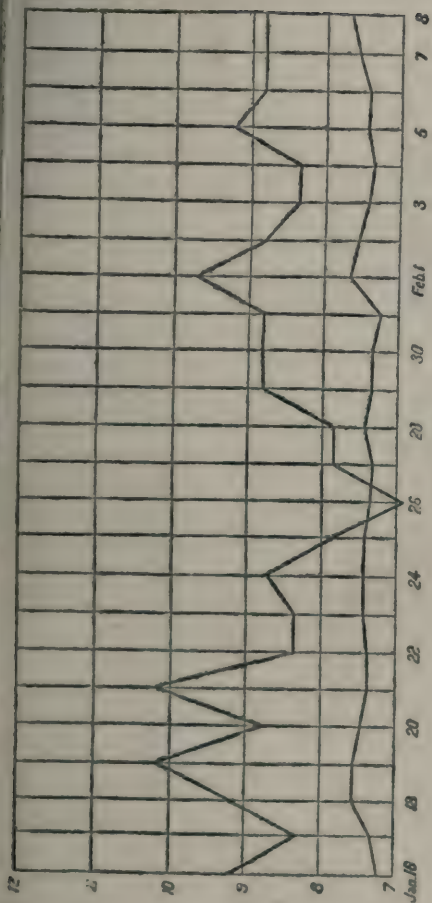


DIAGRAM I.

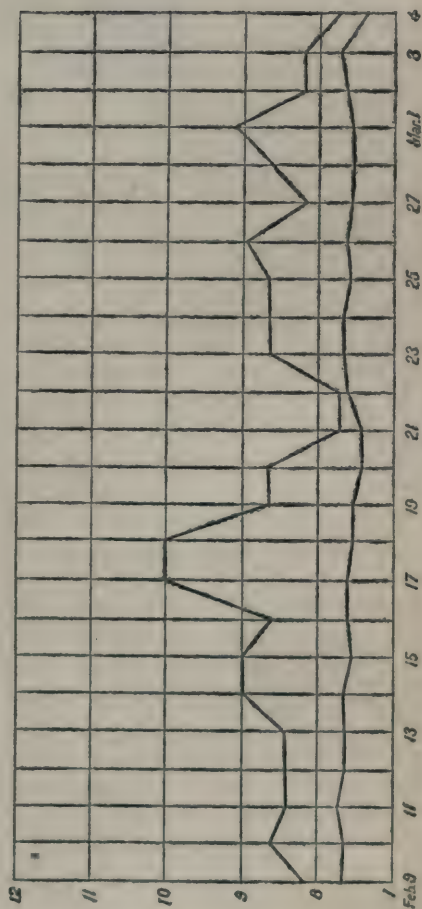
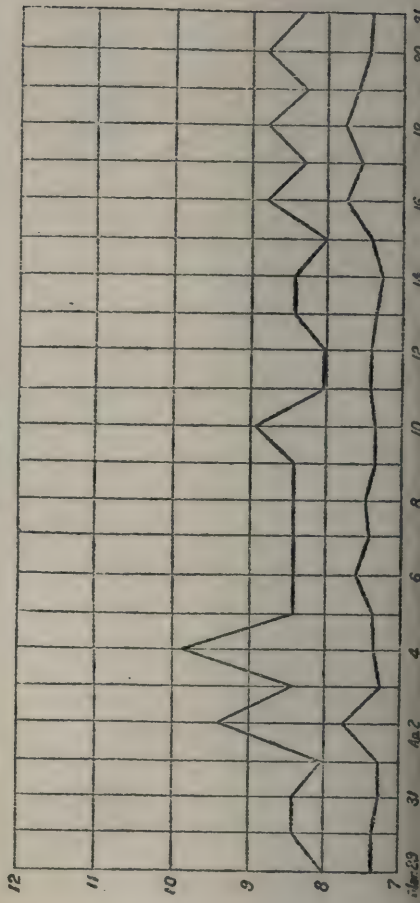
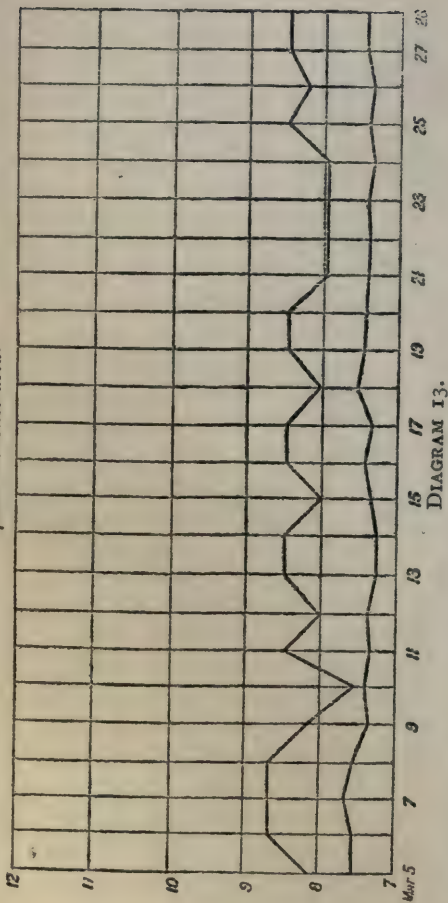


DIAGRAM 12.

FREE AND FIXED CARBONIC ACID IN LONDON WATER, 1904-1905

The figures are in grains per gallon. The upper curve records the free and the lower curve the fixed carbonic acid.



SOFT WATERS

It has already been pointed out that the ultimate destination of the rain-water is determined by permeability or impermeability of the catchment surfaces. Where the impermeability of the rocks is so great that the water runs straight off into rivers or lakes or into catchment basins of the same or similar impervious nature, a soft water is the result. The following analyses are Town Supplies which are little more than rain-waters.

Birmingham

Silica	·12
Oxide of Iron	·14
Sulphate of Lime	·63
Carbonate of Lime	1·11
Chloride of Magnesia	·72
Chloride of Sodium	·74
	<hr/>
	3·46
	<hr/>
Hardness	2·65°

Bolton

Silica	·15
Oxide of Iron	·10
Sulphate of Lime	2·04
Carbonate of Lime	1·11
Sulphate of Magnesia	1·20
Chloride of Sodium	2·05
	<hr/>
	6·65
	<hr/>
Hardness	3·60°

Cardiff

Silica	·16
Oxide of Iron	·14
Sulphate of Lime	1·31
Carbonate of Lime	·84
Chloride of Magnesia	·86
Chloride of Sodium	1·00
	<hr/>
	4·31
	<hr/>
Hardness	2·70°

BOILER CHEMISTRY

Dublin

Silica	·16
Oxide of Iron	·12
Sulphate of Lime	·58
Chloride of Calcium	·61
Chloride of Magnesium	·67
Chloride of Sodium	1·00
	<hr/>
	3·14
	<hr/>
Hardness	1·70°

Dundee

Silica	·14
Oxide of Iron	·09
Sulphate of Lime	·56
Formate of Lime	·94
Formate of Magnesia	·98
Chloride of Sodium	1·23
	<hr/>
	3·94
	<hr/>
Hardness	1·80°

Glasgow

Silica	·06
Oxide of Iron	·03
Sulphate of Lime	·51
Chloride of Calcium	·08
Chloride of Magnesia	·19
Chloride of Sodium	·51
Organic Matter	·76
	<hr/>
	2·14
	<hr/>
Hardness	·65°

Halifax

Silica	·20
Oxide of Iron	·14
Sulphate of Lime	3·81
Chloride of Magnesia	1·00
Chloride of Sodium	1·06
	<hr/>
	6·21
	<hr/>
Hardness	3·85°

Leeds

Silica	·18
Oxide of Iron	·09
Sulphate of Lime	1·75
Carbonate of Lime	1·11
Sulphate of Magnesia	·70
Chloride of Magnesia	·84
Chloride of Sodium	1·00

 5·67

 Hardness 3·85°
Liverpool

Silica	·17
Oxide of Iron	·10
Sulphate of Lime	2·21
Carbonate of Lime	·27
Sulphate of Magnesia	·21
Chloride of Magnesia	·98
Chloride of Sodium	·84

 4·78

 Hardness 3·10°
Manchester

Silica	·18
Oxide of Iron	·11
Sulphate of Lime	1·70
Carbonate of Lime	·27
Nitrate of Lime	·29
Chloride of Magnesia	·62
Chloride of Sodium	1·27

 4·44

 Hardness 2·35°

This water comes from Lake Thirlmere, situated in the Cumberland hills, where the collecting surfaces consist of grits and sandstones which yield very little that is soluble.

Pontypridd

Silica	·17
Oxide of Iron	·22
Sulphate of Lime	·66
Carbonate of Lime	·13
Sulphate of Magnesia	·22
Chloride of Magnesia	·38
Chloride of Sodium	1·37

 3·15

 Hardness 1·18°

These are practically little more than rain-waters collected in catchment basins yielding little or no soluble matters to the rain-water. They of course vary from time to time, but these analyses may be taken as typical examples of these town supplies, and are all soft waters. Many more examples might be given, but the above are sufficient for illustration.

Waters derived from the chalk contain a good deal of matter in solution and are usually hard waters. There are, however, exceptional cases in which soft waters are drawn from wells deep down in the chalk.

WATERS FROM THE CHALK

Brighton

Silica	·17
Oxide of Iron	·10
Carbonate of Lime	14·31
Carbonate of Magnesia	·55
Nitrate of Sodium	2·97
Sulphate of Sodium	·64
Chloride of Sodium	4·10
	<hr/>
	22·84
	<hr/>
Hardness	14·95°

Croydon

Silica	·18
Oxide of Iron	·12
Sulphate of Lime	·48
Carbonate of Lime	14·70
Nitrate of Lime	4·54
Sulphate of Magnesia	1·02
Chloride of Sodium	2·05
	<hr/>
	23·09
	<hr/>
Hardness	18·65°

Eastbourne

Silica	·17
Oxide of Iron	·09
Sulphate of Lime	·39
Carbonate of Lime	13·30
Nitrate of Lime	2·58
Chloride of Calcium	1·14
Chloride of Magnesia	·67
Chloride of Sodium	2·47
	<hr/>
	20·81
	<hr/>
Hardness	16·90°

Erith

Silica	·14
Oxide of Iron	·10
Sulphate of Lime	2·41
Carbonate of Lime	16·79
Nitrate of Lime	2·37
Sulphate of Magnesia	·96
Nitrate of Sodium	2·60
Chloride of Sodium	2·87
	<hr/>
	28·24
	<hr/>
Hardness	20·80°

Lyddon Spout, Kent

Silica	·20
Oxide of Iron	·13
Carbonate of Lime	16·50
Sulphate of Magnesia	·75
Nitrate of Magnesia	1·07
Chloride of Sodium	4·91
	<hr/>
	23·56
	<hr/>
Hardness	17·85°

Snodland, Kent

Silica	·16
Oxide of Iron	·09
Carbonate of Lime	16·79
Nitrate of Lime	2·17
Sulphate of Magnesia	·84
Nitrate of Sodium	2·00
Chloride of Sodium	4·09
	<hr/>
	26·14
	<hr/>
Hardness	18·80°

These waters are all hard waters, the bulk of the hardness being due to carbonate of lime. The carbonates exist in the waters as bicarbonates, but they are given as carbonates as they are resolved into carbonates on boiling. As bicarbonate of lime is decomposed at temperatures of about 200° F., the above method of recording the analyses gives a better idea of what solid matter is likely to be deposited when the water is heated.

Certain natural sands have the property of removing lime and magnesia from water and replacing them by soda. Beds of these

sands are scattered throughout the chalk, and also exist in the limestone formations. They are probably derived from the weathering of older chalk or limestone formations and in some cases are all that remains of pre-existing carboniferous formations. These natural sands are double silicates of alumina and sodium, with a certain amount of water of hydration, and in common with the zeolites, certain lavas and some phonolites possess this somewhat remarkable property of interchanging bases. The zeolites appear to possess this property in the highest degree, but the other-mentioned minerals also possess it.

When hard chalky waters are allowed to filter slowly through these materials, the lime and magnesia are mostly removed and the waters become soft, but as only the bases are exchanged the carbonate of lime becomes carbonate of soda, and as the waters contain much carbonate, the resulting waters become highly alkaline.

Take, for instance, the following example of Kent water:—

Kent Co. Water

Silica	1.12
Oxide of Iron17
Carbonate of Lime	15.04
Nitrate of Lime	6.00
Sulphate of Magnesia	1.65
Chloride of Magnesia55
Chloride of Sodium	2.58

27.11

When this water is passed slowly through a layer of Zeolite, it yields the following water:—

Kent Water passed through Zeolite

Silica67
Oxide of Iron28
Carbonate of Sodium	15.95
Nitrate of Sodium	5.95
Sulphate of Sodium	1.95
Chloride of Sodium	3.28

28.08

Here the lime and magnesia salts have been converted into the corresponding soda salts. The carbonates exist in both cases as bicarbonates, but they have been expressed as carbonates to preserve conformity with the other analyses.

The following is an example of a soft saline water taken deep down in a limestone district :

Analysis

Silica	·30
Oxide of Iron	·09
Carbonate of Lime	1·00
Carbonate of Magnesia	·59
Sulphate of Soda	2·07
Carbonate of Soda	25·20
Chloride of Sodium	2·46
	<hr/>
	31·71
	<hr/>

Hardness 1·70°

Reconstructing this analysis, by substituting lime for soda, the following analysis is obtained :—

Reconstructed Analysis

Silica	·30
Oxide of Iron	·09
Carbonate of Lime	24·78
Sulphate of Lime	1·98
Carbonate of Magnesia	·59
Chloride of Sodium	2·46
	<hr/>
	30·20
	<hr/>

Hardness 27·92°

This is a chalk or limestone water of nearly 28° Hardness. Some of the lime recorded in the reconstructed analysis might have originally existed as magnesia, but as there is no means of arriving at the amount, and the reconstructed analysis is merely given as an illustration, the actual quantity of original magnesia is not of much importance.

This process of interchangeability of bases will therefore account for the presence of soft saline waters in calcareous strata, and will explain how carbonate of soda can get into natural waters, where the strata contains no carbonate of soda. Carbonate of soda as a mineral can hardly be said to exist, it is only found as an efflorescence on the borders of saline lakes, and in very dry or hot climates, where it is evidently produced by the drying up of saline waters. On the other hand, carbonate of lime is widely distributed throughout Nature and occurs in most natural waters.

Silicate of Alumina and Sodium is a constituent of all volcanic

and metamorphic rocks, and many of these partially weathered silicates possess this property of exchanging bases, thus forming an alkaline water and yielding a more calcareous silicate. Calcareous silicates are abundant in Nature and are not so resistant to weathering influences as the sodium aluminium silicates, they therefore disintegrate more rapidly and this process of substitution of bases appears to be one of the steps in the disintegration of the rocks and their ultimate conversion into soil, which is generally little more than silicate of alumina, the other constituents having been removed in the process of weathering.

Other examples of soft waters from the chalk are :—

Kent (Dover)

Silica	1.46
Oxide of Iron20
Carbonate of Lime90
Carbonate of Magnesia63
Sulphate of Soda	2.45
Carbonate of Soda	28.81
Chloride of Sodium	7.37
	<hr/>
	41.82
	<hr/>
Hardness	1.65°

London

Silica42
Carbonate of Lime	3.41
Carbonate of Magnesia	1.51
Nitrate of Sodium22
Sulphate of Sodium	18.65
Carbonate of Sodium	13.63
Chloride of Sodium	18.43
	<hr/>
	56.27
	<hr/>
Hardness	5.21°

MAGNESIAN WATERS

When waters contain any considerable amount of magnesia, the magnesia is generally derived from the magnesium limestones, or from the infiltration of sea-water, either into the wells or rivers. Certain strata also contain polyhalite beds and other similar formations formed by the drying up of ancient seas, and these formations can and do yield considerable quantities of sulphate and chloride of magnesia to any water which may come into contact with them.

There is a belt of the magnesium limestones about 120 miles long and 10–20 miles broad beginning at Nottingham and ending in the neighbourhood of Durham, and is a very conspicuous blue patch on the geological map of England. Waters which have been affected by percolation through any of the formations of this belt are generally found to contain considerable quantities of magnesia, deep well-waters especially. Waters from the chalk seldom contain as much as 1 grain of magnesia per gallon; in the districts between Nottingham and Durham the amount of magnesia is generally very much higher. Examples:—

Doncaster. Well

Silica	·18
Oxide of Iron	·13
Sulphate of Lime	13·76
Carbonate of Lime	19·61
Nitrate of Lime	2·43
Sulphate of Magnesia	21·51
Chloride of Magnesia	1·15
Chloride of Sodium	3·10

61·87

Hardness 47·10°

Nottingham

Silica	·42
Oxide of Iron	·08
Carbonate of Lime	21·69
Carbonate of Magnesia	9·39
Sulphate of Sodium	1·14
Carbonate of Sodium	6·72
Chloride of Sodium	4·50

43·94

Hardness 32·87°

Nottingham Town

Silica	·16
Oxide of Iron	·09
Sulphate of Lime	1·67
Carbonate of Lime	1·29
Nitrate of Lime	4·98
Carbonate of Magnesia	5·50
Chloride of Sodium	2·05

15·74

Hardness 12·10°

Nottingham. Well

Silica	·20
Oxide of Iron	·17
Sulphate of Lime	16·20
Carbonate of Lime	23·79
Sulphate of Magnesia	23·20
Nitrate of Magnesia	1·78
Nitrate of Sodium	·94
Chloride of Sodium	13·92
	<hr/>
	80·20
	<hr/>
Hardness	56·30°

RIVER-WATERS

The character of a river-water will be determined by the geological nature of the ground from which it receives its supplies. Thus the river Dee (Scotland), flowing through granite districts, is soft and contains but little matter in solution. The Thames, receiving much of its supply from the chalk, is a hard carbonate water; and the Trent, being fed by streams flowing through the magnesium limestone district, contains considerable quantities of magnesia. The flow of the tide can bring in sea-water, but the following examples are taken from the rivers beyond this influence.

River Dee at Aberdeen

Silica	·16
Oxide of Iron	·11
Sulphate of Lime	·97
Carbonate of Lime	·68
Chloride of Magnesia	·66
Chloride of Sodium	·82
	<hr/>
	3·40
	<hr/>
Hardness	2·10°

River Don at Sheffield

Silica	·24
Oxide of Iron	·18
Sulphate of Lime	9·66
Sulphate of Magnesia	5·82
Sulphate of Sodium	3·12
Chloride of Sodium	3·69
	<hr/>
	22·71
	<hr/>
Hardness	11·95°

River Irwell (Radcliffe)

Silica	·23
Oxide of Iron	·19
Sulphate of Lime	6·11
Carbonate of Lime	8·82
Sulphate of Magnesia	4·32
Sulphate of Sodium	6·34
Chloride of Sodium	9·00

 35·01

Hardness 16·90°

River Thames at Egham

Silica	·23
Oxide of Iron	·14
Sulphate of Lime	·22
Carbonate of Lime	17·20
Sulphate of Magnesia	1·32
Nitrate of Sodium	1·78
Sulphate of Sodium	1·99
Chloride of Sodium	2·87

 25·75

Hardness 18·50°

River Trent at Newark

Silica	·23
Oxide of Iron	·15
Sulphate of Lime	7·77
Carbonate of Lime	12·89
Sulphate of Magnesia	8·16
Nitrate of Sodium	1·78
Sulphate of Sodium	4·01
Chloride of Sodium	6·96

 41·95

Hardness 25·40°

Rivers are of course liable to pollution, from works and factories on or immediately adjacent to them, but cases of pollution are exceptional and are generally drastically dealt with by the Pollution Authorities. Laws are laid down as to what is and what is not pollution. In cases where manufacturers are allowed to use the river-waters for manufacturing purposes other than for use in boilers, stringent conditions are usually attached to this permission, and treatment of the used water has generally

CURVE SHOWING THE VARIATION IN HARDNESS OF A DEEP WELL WATER DURING A PERIOD OF TWO YEARS.

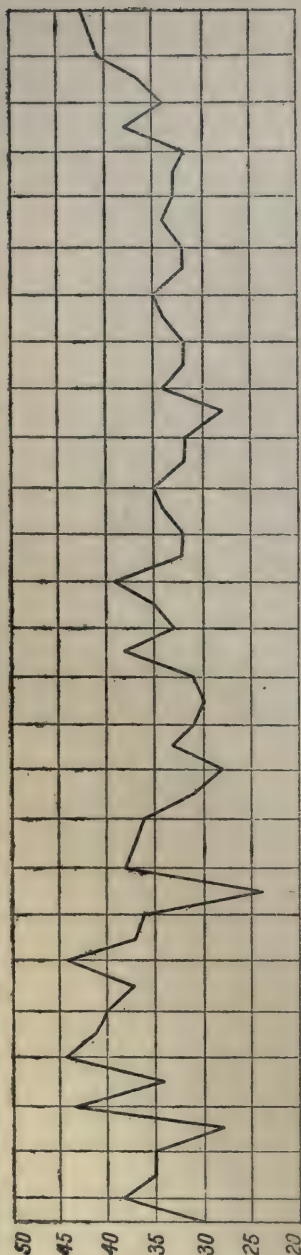


DIAGRAM 15.

to be resorted to before the users are allowed to put it back into the rivers. The following is possibly exceptional, but it is a bad case of pollution by Sulphuric Acid.

River Don at Sheffield

Silica	·20
Oxide of Iron	·86
Sulphate of Lime	6·65
Sulphate of Magnesium	5·04
Nitrate of Sodium	1·48
Chloride of Sodium	3·28
Sulphuric Acid	2·20

19·71

Hardness 9·10°

DEEP WELLS

Deep well-waters are not so liable to variation as shallow well-waters, but obviously the composition of the water is dependent upon the strata from which the water is drawn. When the well is partially exhausted by pumping, water may be drawn, or forced into the well from directions other than those usually obtaining, and the water occasionally change its character entirely. More frequently, however, the change is merely one of quantity of impurities and not of variation in character. The accompanying diagram shows the variations in a deep well at Birmingham, during a period of two years. The samples were taken twice each month.

SURFACE WELLS

Shallow or surface wells, which practically only drain the upper surfaces of the ground, vary greatly from day to day, and can never be relied upon. After rain they may be in good condition, while at other times they are extremely bad. Of the following examples, the first two give some idea of the variation in a shallow well. The samples were taken from the same well at different times.

Isleworth, 1908

Silica	·22
Oxide of Iron	·17
Sulphate of Lime	12·55
Nitrate of Lime	16·05
Carbonate of Lime	2·79
Sulphate of Magnesia	8·76
Nitrate of Sodium	5·66
Chloride of Sodium	9·42
	<hr/>
	55·62
	<hr/>
Hardness	29·10°

Isleworth, 1917

Silica	·16
Oxide of Iron	·11
Sulphate of Lime	60·57
Nitrate of Lime	27·44
Sulphate of Magnesia	30·00
Nitrate of Sodium	51·92
Chloride of Sodium	26·62
	<hr/>
	196·82
	<hr/>
Hardness	97·0°

Surface Well, East Sheen

Silica	·33
Oxide of Iron	·20
Sulphate of Lime	42·74
Carbonate of Lime	8·95
Nitrate of Lime	28·80
Sulphate of Magnesia	7·14
Nitrate of Sodium	44·60
Chloride of Sodium	11·87
	<hr/>
	144·63
	<hr/>
Hardness	62·05°

Peterborough

Silica	62
Oxide of Iron	14
Sulphate of Lime	95.88
Sulphate of Magnesia	27.57
Carbonate of Magnesia	4.07
Sulphate of Sodium	19.63
Chloride of Sodium	26.21
	<hr/>
	174.12
	<hr/>
Hardness	98.32°

The following are analyses of two wells in the same works, one a surface well, the other a deep well.

Surface Well

Silica	23
Ferrous Carbonate	9.02
Sulphate of Lime	59.28
Carbonate of Lime	23.22
Sulphate of Magnesia	11.82
Nitrate of Magnesia	2.59
Chloride of Magnesia	5.37
Chloride of Sodium	24.00
	<hr/>
	135.53
	<hr/>
Hardness	84.03°

Deep Well

Silica	43
Oxide of Iron	99
Carbonate of Lime	2.50
Carbonate of Magnesia	1.60
Sulphate of Sodium	13.38
Carbonate of Sodium	17.60
Chloride of Sodium	14.33
	<hr/>
	49.93
	<hr/>
Hardness	4.42°

Although these samples are taken from the same spot at different depths, they vary very widely in character, the one is a hard sulphate-water, the other a soft alkaline soda-water.

CANAL-WATERS

Canal-waters, like river-waters, are largely influenced by the land through which they run, but unlike river-waters, any

pollution is likely to be more permanent, as there is little flow to carry the impurities away. The only disturbance is caused by passing barges and by loss of water through the locks. Any impurities that are put into a canal are therefore likely to remain near the source of pollution, and will persist for some time.

Birmingham Canal, 1909

Silica	·20
Oxide of Iron	·19
Sulphate of Lime	7·70
Carbonate of Lime	7·70
Sulphate of Magnesia	8·04
Nitrate of Sodium	3·57
Sulphate of Sodium	3·75
Chloride of Sodium	12·28
	<hr/>
	43·43
	<hr/>
Hardness	20·06°

1917

Silica	·32
Oxide of Iron	1·44
Sulphate of Lime	56·30
Carbonate of Lime	·69
Sulphate of Magnesia	17·28
Nitrate of Sodium	20·82
Sulphate of Sodium	12·99
Chloride of Sodium	81·90
	<hr/>
	191·74
	<hr/>
Hardness	50·33°

The 1917 sample contained a good deal of organic matter and traces of picric acid in addition to the mineral matters.

Grand Junction Canal

Silica	·25
Oxide of Iron	·19
Sulphate of Lime	22·58
Carbonate of Lime	·41
Carbonate of Magnesia	7·41
Nitrate of Sodium	1·49
Chloride of Sodium	6·14
	<hr/>
	38·47
	<hr/>
Hardness	25·83°

BOILER CHEMISTRY

Leamington Canal

Silica	·19
Oxide of Iron	·16
Sulphate of Lime	3·28
Carbonate of Lime	10·90
Sulphate of Magnesia	6·12
Sulphate of Sodium	2·24
Chloride of Sodium	2·87
	<hr/>
	25·76
	<hr/>
Hardness	18·40°

Manchester Ship Canal

Silica	·28
Oxide of Iron	·20
Sulphate of Lime	·63
Carbonate of Lime	14·54
Sulphate of Magnesia	5·94
Sulphate of Sodium	12·60
Chloride of Sodium	14·33
	<hr/>
	48·52
	<hr/>
Hardness	19·95°

Regent's Canal

Silica	·24
Oxide of Iron	·17
Sulphate of Lime	5·17
Carbonate of Lime	14·00
Sulphate of Magnesia	9·63
Chloride of Magnesia	5·98
Nitrate of Sodium	2·97
Chloride of Sodium	74·50
	<hr/>
	112·66
	<hr/>
Hardness	32·05°

S. Staffordshire Canal

Silica	·20
Oxide of Iron	·19
Sulphate of Lime	10·10
Carbonate of Lime	18·47
Sulphate of Magnesia	17·76
Sulphate of Sodium	23·67
Nitrate of Sodium	2·38
Chloride of Sodium	27·03
	<hr/>
	99·80
	<hr/>
Hardness	40·70°

Walsall Canal

Silica	25
Oxide of Iron	19
Carbonate of Lime	26.70
Carbonate of Magnesia	1.07
Sulphate of Magnesia	20.58
Nitrate of Sodium	1.49
Sulphate of Sodium	58.66
Chloride of Sodium	15.56

124.50

Hardness 48.10°

Wigan Canal

Silica	25
Oxide of Iron	18
Sulphate of Lime	29.82
Carbonate of Lime	8.68
Sulphate of Magnesia	22.86
Sulphate of Sodium	73.34
Chloride of Sodium	45.86

180.99

Hardness 49.65°

COLLIERY WATERS

Colliery waters differ considerably; some are good soft waters, some are acid, some extremely alkaline, and others are charged with an excessive amount of soda salts.

Colliery near S. Hetton

Silica	24
Carbonate of Manganese	1.64
Carbonate of Lime	12.59
Sulphate of Lime	36.20
Sulphate of Magnesia	52.50
Sulphate of Sodium	102.40
Chloride of Sodium	155.61

361.18

Hardness 83.30°

The scale from this water contained 15.71 per cent. of Oxide of Manganese.

BOILER CHEMISTRY

Colliery near Llanelly

Silica	·15
Oxide of Iron	·11
Sulphate of Lime	·27
Carbonate of Lime	3·50
Sulphate of Magnesia	1·26
Nitrate of Sodium	·60
Chloride of Sodium	2·86
	<hr/>
	8·75
	<hr/>
Hardness	4·75°

Colliery near Wakefield

Silica	·12
Oxide of Iron	·09
Carbonate of Lime	·55
Carbonate of Magnesia	·74
Carbonate of Sodium	30·08
Sulphate of Sodium	20·39
Chloride of Sodium	39·72
	<hr/>
	91·69
	<hr/>
Hardness	1·43°

Colliery near Wakefield

Silica	·27
Oxide of Iron	·08
Sulphate of Lime	16·51
Sulphate of Magnesia	3·48
Carbonate of Magnesia	14·48
Sulphate of Sodium	20·40
Chloride of Sodium	10·65
	<hr/>
	65·87
	<hr/>
Hardness	32·30°

These waters are both from the same colliery, though taken from different seams, one is a soft soda-water, the other a hard water, containing considerable quantities of lime and magnesia.

Colliery at Whitehaven

Silica	·14
Oxide of Iron	·10
Sulphate of Lime	1·21
Carbonate of Lime	2·09
Sulphate of Magnesia	·31
Chloride of Magnesia	·26
Chloride of Sodium	2·54
	<hr/>
	6·65
	<hr/>
Hardness	3·30°

Pit Water

Silica	·25
Oxide of Iron	·17
Sulphate of Lime	33·76
Carbonate of Lime	9·79
Sulphate of Magnesia	38·16
Sulphate of Sodium	23·96
Chloride of Sodium	11·05

117·14

Hardness	66·40°
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Colliery near Derby

Silica	·65
Oxide of Iron	·07
Carbonate of Lime	11·39
Carbonate of Magnesia	7·10
Sulphate of Sodium	38·43
Nitrate of Sodium	1·78
Carbonate of Sodium	21·10
Chloride of Sodium	110·56

191·08

Hardness	19·84°
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Colliery near Nuneaton

Silica	·67
Oxide of Iron	·09
Carbonate of Lime	22·80
Carbonate of Magnesia	11·76
Sulphate of Sodium	59·50
Carbonate of Sodium	27·76
Chloride of Sodium	286·65

409·23

Hardness	36·80°
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Pit Water

Silica	·75
Oxide of Iron	·10
Carbonate of Lime	2·30
Carbonate of Magnesia	1·72
Nitrate of Sodium	2·97
Sulphate of Sodium	19·30
Carbonate of Sodium	76·30
Chloride of Sodium	49·05

152·49

Hardness	4·35°
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PEATY WATERS

Waters which penetrate into peat are often acid, and in making an analysis of these waters it sometimes happens that there is an insufficiency of mineral acids to satisfy all the bases. In this case it has to be assumed that some of the lime and magnesia is combined with some organic acid or acids. Very little is known as to the character and composition of these acids, but distilled water bottled up with peaty matter soon acquires decided acid characters. When the water is brownish or yellow coloured there is reason to suppose that the acids are humic acids. In other cases the water is colourless and gives reactions which would be expected from a very dilute solution of formic acid or glycollic acid. These acids are all derived from peat, and peat itself is little else than cellulose in a more or less partial state of disintegration. Cellulose is represented by the formula $n(C_6H_7O_5)(HO)_3$, and each of the Hydroxyl groups (HO) are replaceable by nitric, acetic or formic acids. By complete oxidation the cellulose would be converted into carbonic acid and water, but there are many intermediate stages in the process, one of which appears to be the formation of formyl-cellulose $n(C_6H_7O_5(CHO)_3)$. This is a process of oxidation in which the carbon is converted into Formic Acid (CH_2O_2), an acid corresponding to carbon monoxide.

This formyl-cellulose is apparently only very slightly soluble in water and can only exist in soft waters. Water containing it is sometimes very slightly acid or on the border-line between acidity and alkalinity. Such a water contains no carbonic acid and has a corrosive action upon lead, zinc and iron pipes. It also takes up oxygen from a solution of permanganate of potash, showing the substance in the water to be only in a partial state of oxidation. The water yields a volatile acid when boiled, and this distillate, though very dilute, shows the characteristics of formic acid. When treated with a measured quantity of lime-water in the cold and allowed to stand, a straw-coloured deposit settles out, the water loses 80 per cent. of its permanganate destroying power and at the same time no longer yields an acid distillate on boiling. There is also a disappearance of much of the added lime; it is not found in solution but has come down in the deposit. This also takes place when the water is shaken up with calcium hydrate. The disappearance of the lime taken in conjunction with the loss of oxygen-absorbing power

can apparently only have been brought about by the lime combining with the formyl-cellulose and bringing it down as an insoluble straw-coloured precipitate. The precipitate cannot be formate of lime, because this salt is soluble in water. It is not at all improbable that bacterial action is the cause of the partial oxidation of the peat and the production of formic acid. It is also probable that the precipitating action of lime on the hydrolized or partially oxidized cellulose removes the medium upon which the bacteria thrive, and may be the reason why "the excess lime" treatment has a sterilizing action on certain waters containing organic pollution. Soda does not form this insoluble deposit, and this may explain why lime is a bactericide and soda not.

Other waters from similar sources although they do not contain the partially oxidized cellulose contain the acids derived from it. The following analysis gives the composition of such a water. It is quite soft, but is slightly acid.

Belfast

Silica	·10
Oxide of Iron	·12
Formate of Lime	1·04
Sulphate of Magnesia	·66
Chloride of Sodium	·80
Formic Acid	·64
	<hr/>
	3·36
	<hr/>

The acid can be neutralized by passing the water slowly through a filter packed with limestone or marble. The water so treated contains :—

Silica	·10
Oxide of Iron	·12
Formate of Lime	2·07
Carbonate of Lime	·63
Sulphate of Magnesia	·66
Chloride of Sodium	·80
	<hr/>
	4·38
	<hr/>

SEA-WATER

The principal constituents of sea-water are chloride of sodium, chloride and sulphate of magnesium, and sulphate of lime. There are also smaller quantities of carbonate of lime, bromide of

magnesium and chloride of potassium. As for all practical purposes the amounts of bromine and potassium are exceedingly small compared to the others, in some only of the following analyses have they been estimated. In the other analyses the bromine is included with the chlorine and the potassium with the sodium. The average amount of chlorine may be taken as 1300 grains per gallon, which is equivalent to 2140 grains of chloride of sodium, but the amount of soluble material in sea-water varies slightly all over the world. Where there is much fresh water coming down to the sea, the water will of course not contain quite so much total solids, and where there is no fresh water the total solids will be slightly higher. These differences are gradually adjusted by tides and currents and other physical influences. The following are analyses of sea-water taken in various parts of the world. The figures are in grains per gallon.

Gulf of Mexico

Silica	24
Oxide of Iron	15
Sulphate of Lime	101.20
Carbonate of Lime	8.75
Chloride of Magnesia	239.02
Bromide of Magnesia	20.24
Chloride of Potassium	55.30
Chloride of Sodium	1928.97
	<hr/>
	2353.87

Mediterranean

Silica	25
Oxide of Iron	13
Sulphate of Lime	101.27
Carbonate of Lime	6.29
Chloride of Magnesia	262.48
Bromide of Magnesia	12.88
Sulphate of Magnesia	179.40
Chloride of Sodium	2207.44
	<hr/>
	2770.14

Falkland Islands

Silica	22
Oxide of Iron	14
Sulphate of Lime	88.96
Carbonate of Lime	6.59
Chloride of Magnesia	240.05
Sulphate of Magnesia	153.34
Chloride of Sodium	2079.47
	<hr/>
	2568.77

In the last analysis the bromine was not determined and is included in the chloride of sodium.

TIDAL WATERS

Where rivers are liable to be affected by the ebb and flow of the tide, more or less sea-water will be mixed with the river-waters, and if the amount does not entirely prevent their use as feed waters for boilers, nevertheless it renders their character so variable that it is at all times dangerous to use them for this purpose. Below are a few analyses of waters taken from rivers within the influence of the tides.

Devonport

Silica	·26
Oxide of Iron	·17
Sulphate of Lime	81·48
Carbonate of Lime	8·40
Sulphate of Magnesia	156·19
Chloride of Magnesia	214·46
Chloride of Sodium	1988·20
	<hr/>
	2449·16
	<hr/>

Thames at Vauxhall

HIGH TIDE

Silica	·23
Oxide of Iron	·19
Carbonate of Lime	13·19
Carbonate of Magnesia	·43
Sulphate of Magnesia	2·52
Nitrate of Sodium	2·38
Sulphate of Sodium	1·83
Chloride of Sodium	8·60
	<hr/>
	29·37
	<hr/>

Hardness 15·80°

LOW TIDE

Silica	·24
Oxide of Iron	·20
Sulphate of Lime	·73
Carbonate of Lime	14·27
Sulphate of Magnesia	1·86
Nitrate of Sodium	1·78
Sulphate of Sodium	1·06
Chloride of Sodium	3·27
	<hr/>
	23·41
	<hr/>

Hardness 16·35°

Wear at Sunderland

Silica	25
Oxide of Iron	14
Sulphate of Lime	58.67
Carbonate of Lime	13.19
Sulphate of Magnesia	56.43
Chloride of Magnesia	104.64
Nitrate of Sodium	1.45
Chloride of Sodium	894.40
	<hr/>
	1129.17
	<hr/>

In cases where the rivers are large and drain enormous tracts of country, and where there is a rainy and a dry season, the tide is often pushed back in the rainy season by the flood of fresh water brought down by the rivers. In the dry season the tide recovers its position, and parts of the river which were quite fresh in the rainy season become salt or brackish in the dry season. This fact is of considerable importance to power stations which draw their supply from the rivers upon which they are situated. The plant which is designed for use with a good and comparatively soft water works well for a time, then troubles begin, last for a time and then disappear again. It is often thought that these have been overcome, but they only break out again and the plant is blamed as being unsatisfactory. If it had been realized that these intermittent troubles were due to sea-water finding its way into the boilers, those on the spot would know how to deal with the difficulties as they arise. In designing boiler plants for use in such positions it should always be realized that places which are considered to be well above the influence of the tide can be affected in this way. How far above the ordinary reach of the tide this influence makes itself felt it is impossible to say, but it will of course depend upon the volume of water brought down by the rivers in the dry and the wet seasons. In designing the plant care should be taken that the water samples upon which the scheme is based should be taken both in the dry and wet seasons.

The accompanying diagram shows the amount of sea-water in the River Para during the months November to March. Being south of the equator, March would correspond to the wet season, when the water is quite normal and only contains the normal amount of chlorides. November, which would correspond to our summer season, would be comparatively dry, and with less

water coming down the tide would flow up further, and introduce a certain amount of salt into water which had previously been quite fresh. This diagram also shows the variations between the two extremes.

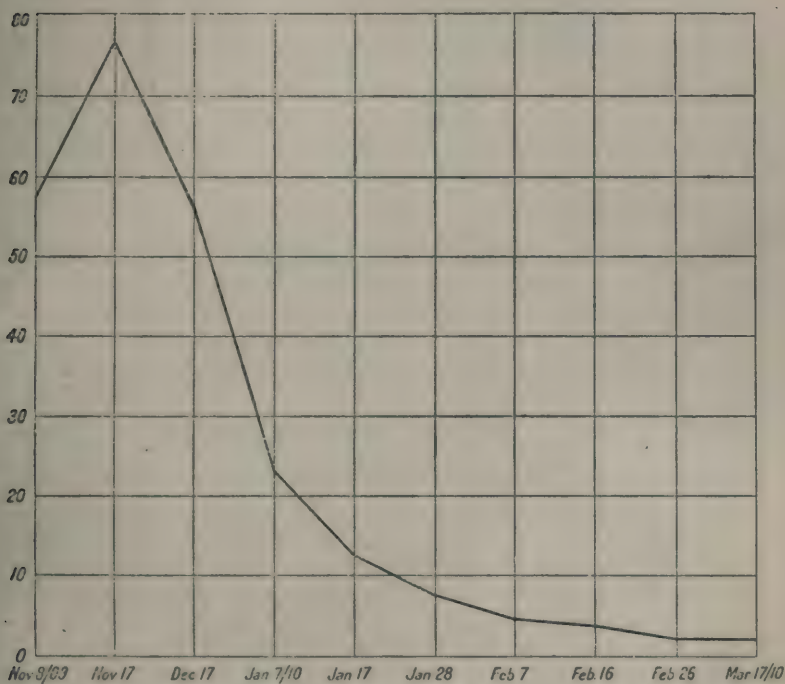


DIAGRAM 16.

CHAPTER II

ACIDS, BASES AND SALTS

BODIES such as sulphate of lime, nitrate of magnesia, etc., are called salts, as they are bodies analogous to chloride of sodium which is known as common salt. Whatever theoretical view of the constitution of these salts may be taken, for all practical purposes no serious error can be committed in regarding them as being composed of two dissimilar bodies having opposite characters. These two bodies having exactly opposite properties, when combined in certain definite proportions produce a third body possessing the properties of neither, and having distinctive characters of its own. This third body is generally called a salt, and its component parts are called acid or basic radicles respectively, or for the sake of brevity, acids and bases.

The commoner acids are bodies which have a sour taste, cause effervescence when brought into contact with carbonates and turn blue litmus red. The bases which are soluble in water, on the other hand, do not have this sour taste, do not cause effervescence with carbonates, and do not turn blue litmus red, but on the contrary turn red litmus blue. These two classes of bodies, therefore, have exactly opposite properties so far as litmus is concerned. By their combination in certain proportions they produce third bodies in which the above-mentioned properties are missing, and which possess distinct characters of their own.

When an acid is combined with a base in certain proportions, so as to leave no excess of either, the resultant body may have no taste at all, or may have a taste dissimilar to its components; it will cause no effervescence with carbonates, and is perfectly indifferent to litmus; that is, it neither changes blue litmus to red nor red litmus to blue, the original colour, whatever it was, remaining the same. For example, sulphuric acid is a powerful acid possessing all the properties of an acid as above described. Lime, on the other hand, possesses all the opposite properties,

yet when they are mixed in certain definite proportions the resultant body is a tasteless inert material. It is sulphate of lime, and as it contains an acid and a base is regarded by chemists as a salt.

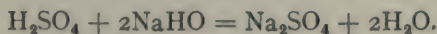
It does not follow that all salts are neutral bodies, that is, indifferent to litmus and other indicators. They may be strongly acid, or, on the other hand, strongly basic. When they are strongly basic and at the same time soluble in water they are said to be alkaline. Alkalinity, strictly speaking, refers to the bases themselves which are soluble in water, but as salts such as carbonate of soda and carbonate of potash perform many of the functions of these bases, they are commonly, if erroneously, called alkalies.

Carbonate of soda is a highly alkaline salt and its solution is said to be alkaline. The carbonic acid, which is the acid part of the salt, is a very weak acid and is not sufficiently strong to destroy the strongly alkaline properties of the basic or soda portion of the salt, hence the characters of the soda predominates and the salt is alkaline. On the other hand, sulphuric acid being a strong acid is sufficiently strong to destroy the alkaline nature of the soda, and sulphate of soda is a neutral salt.

Sulphuric Acid (H_2SO_4) contains two atoms of hydrogen. These hydrogen atoms can be separately neutralized or replaced by soda, thus:—



and



In the former case the quantity of soda taken up is not sufficient to destroy the acid characters of the sulphuric acid, hence the salt formed is strongly acid. It not only has a sour taste, but will cause effervescence with carbonates and turn blue litmus red. This salt is bisulphate of soda, often called the acid sulphate.

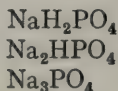
The other sulphate or normal sulphate is quite neutral, the double amount of soda taken up being sufficient to destroy the acid properties of the original sulphuric acid.

When an acid has two atoms of replaceable hydrogen, as in the case of sulphuric acid, the acid is said to be dibasic, and there are two classes of its salts, the acid and the normal. Carbonic acid, like sulphuric acid, is a dibasic acid, hence there are two classes of carbonates, the acid or bicarbonates, and the normal

carbonates. Thus NaHCO_3 is the bicarbonate and Na_2CO_3 the normal carbonate.

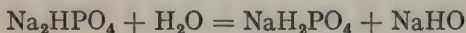
Hydrochloric Acid (HCl) has only one atom of hydrogen, hence there can only be one class of chlorides, the normal chlorides. As Nitric Acid (HNO_3) has also only one atom of hydrogen, the only nitrates are the normal nitrates.

Phosphoric Acid (H_3PO_4) has three atoms of hydrogen all of which are replaceable by metals, hence there are three classes of phosphates :—

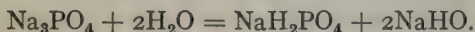


known respectively as mono-, di- and trisodic phosphates.

The monophosphate of soda is an acid salt; the other two, the diphosphate and the triphosphate, are neutral when dissolved in a small quantity of water, but when treated with a large quantity of water both these salts are resolved into acid salt and caustic soda is set free.



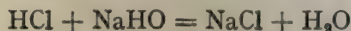
and



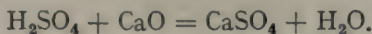
It is this caustic soda which is useful when phosphate of soda is used in water treatment. The tribasic phosphate sets free two equivalents of caustic soda as against one set free by the ordinary commercial or orthophosphate (Na_2HPO_4), and is for this reason a more useful salt than the orthophosphate in treating water.

As the ordinary phosphate of soda crystallizes with twelve molecules of water, it contains 60 per cent. of water and is therefore an expensive source of caustic soda. The triphosphate has the formula $\text{Na}_3\text{PO}_4 \cdot 10\text{H}_2\text{O}$, and when pure contains 52·32 per cent. of water. A sample of the commercial article known as "tripsa" contained 52·37 per cent. of water, and when largely diluted with water set free 22·8 per cent. of caustic soda, as against 23·26 per cent. demanded by theory. This means that each lb. of the commercial article develops 3·65 oz. of caustic soda.

When hydrochloric acid acts upon caustic soda the reaction can be expressed by the equation :—



and sulphuric acid upon lime thus :—



In this case the sulphuric acid has parted with the elements of water and only a portion of the sulphuric acid, viz. the SO_3 , has entered into the constitution of the sulphate of lime, and in the case of hydrochloric acid only a part of the soda and a part of the hydrochloric acid have entered into the chloride of soda formed. For this reason it is not strictly accurate to say that chloride of calcium is a salt consisting of lime and hydrochloric acid. This may be got over by saying that in this case the metal is the base and chlorine the acid, and that with sulphate of lime the calcium is the base and the SO_4 the acid. But whichever view be taken, there are two bodies of opposite characteristics which enter into the constitution of the salt. And as both these salts are in reality produced by the combination of a metal with the corresponding acid, it will make for simplicity if, with salts containing no oxygen, the metal is considered to be the base and the remaining element the acid, and in the cases where the salt does contain oxygen, that the salt is composed of a base which is the oxide of a metal and a group of other elements which may be called the acid radicle. Thus sulphate of lime may be expressed as CaOSO_3 where oxide of calcium is the base and SO_3 the acid radicle.

Although a salt may be very soluble in water, it does not follow that its component parts are soluble. For instance, oxide of zinc is insoluble in water, but sulphate of zinc is very soluble; and again, magnesia is practically insoluble in water, but chloride and nitrate of magnesia are soluble to an almost unlimited extent.

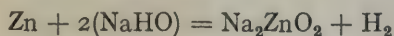
Lime is only slightly soluble in water, and sulphate of lime only to a slightly greater extent than lime, whereas chloride of calcium is an exceedingly soluble salt, so that the properties of a salt do not as a rule correspond with the properties of its constituents. As a further example, silver oxide is insoluble in water, but sulphate of silver is fairly soluble and chloride of silver insoluble. Barium, on the other hand, forms a soluble chloride but an insoluble sulphate, and a knowledge of these properties of the various elements are the foundations upon which many chemical operations and processes are based.

To arrive at the real nature of an acid, the general conception that it is a corrosive substance having a sour taste, and burns

one's clothes, must be greatly modified. The commoner acids, such as sulphuric, nitric and hydrochloric, do possess these properties, but there are many other bodies in reality acids which do not possess these properties and only become acids under certain conditions.

At ordinary temperatures Silica is an inert tasteless substance, almost insoluble in anything but hydrofluoric acid. But if finely powdered silica is heated with sulphate of soda, the silica expels the sulphuric acid and a new salt, viz. silicate of soda, is formed. Here silica at high temperatures expels a powerful acid like sulphuric acid. On the other hand, if sulphuric acid be added to a solution of silicate of soda, the sulphuric acid turns out the silica in the form of a precipitate and forms sulphate of soda. The same thing is true of carbonic acid. If silica is heated with carbonate of soda, carbonic acid is expelled and silicate of soda formed; and when a solution of silicate of soda is treated with a stream of carbonic acid, carbonate of soda is formed and silica precipitated. As sulphuric and carbonic acids are generally recognized as acids, silica, which will turn them both out at high temperatures, must also be considered to be an acid, and the ordinary definition of an acid must be modified if the true character of an acid is to be realized.

Again, many metals which are usually the basic parts of a salt can play the part of an acid. Zinc, which forms salts in which it plays the part of the base, can be made to play the part of an acid. Thus in zinc sulphate the zinc or oxide of zinc is the base and sulphuric acid the acid. But if zinc be heated with Caustic Soda the zinc expels the hydrogen and forms an alkaline salt called zincate of soda, thus :—



or the same salt can be obtained by heating NaHO and ZnO. Not only does oxide of zinc act in this way, but oxide of iron, which is usually strongly basic, can be made to play the part of an acid and forms salts known as ferrites ($\text{M}_2\text{Fe}_2\text{O}_4$ or $\text{M}_2\text{OFe}_2\text{O}_3$). Aluminium, chromium and manganese, which have strongly marked metallic characters, also can be made to play the part of acids, and the best known and most industrially useful preparations of the two latter metals are the salts in which they act the part of acids. Manganate or permanganate of potash and bichromate of potash are much more useful materials industrially than any other of the salts of these metals. On the other hand,

although aluminate of soda is a commercial article, aluminium is more widely known and used in the form of alum or sulphate of alumina, that is, in a form in which the aluminium takes the form of the base. These examples can be carried still further, for not only do the oxides of some metals play the part of acids, but the metal may enter into a more complex group which will form salts, in which the group acts as an acid. Thus iron can be united with carbon and nitrogen into a group known as ferrocyanogen ($\text{Fe}(\text{CN})_2$), and this group or radicle forms salts known as ferrocyanides, the most characteristic of which are the ferrocyanides of sodium and of potassium ($\text{Na}_4\text{Fe}(\text{CN})_6$ or $\text{K}_4\text{Fe}(\text{CN})_6$). These ferrocyanides or prussiates can be made the starting point for preparing the ferrocyanides of many other metals, and ferrocyanic acid itself ($\text{H}_4\text{Fe}(\text{CN})_6$), can be isolated. Ferrocyanic acid possess distinct acid properties; it is strongly acid to litmus and turns out the acids from carbonates, acetates and oxalates, and neutralizes alkalies.

These instances show that at first sight it is not always possible to say whether any given substance is an acid or not, and also show that many substances which are not usually acids can under certain conditions be made to play the part of an acid, and that even strong bases such as oxide of zinc may enter into the constitution of a salt as the acid radicle.

Many substances, although they may not under ordinary circumstances be acids, may, however, be potential acids, and conditions may arise in which they may do the work of acids, and if they do this work should be recognized as acids. Silica must be considered a potential if not an actual acid, and in a boiler conditions may be allowed to arise in which silica can cause corrosion. If it does not directly cause the corrosion, nevertheless it is the cause of sulphuric acid or phosphoric acid or nitric acid being in a position to do the corrosion, by turning these acids out of their previous combinations. It has been mentioned that silica will turn sulphuric acid out of sulphate of soda, it will also turn it out from sulphate of lime. If the sulphate of lime exists as a boiler scale and the water also deposits silica, such a scale when heated to a high temperature, as it certainly would be if any thickness of this scale is formed, will develop sulphuric acid and in this way cause corrosion. Although silica itself cannot corrode nor can even be suspected of doing so, nevertheless it is the direct cause of the corrosion, for without it no sulphuric acid would be set free.

ACIDITY AND ALKALINITY IN WATERS

When dealing with the question of acidity in natural waters it is often difficult to say whether any particular water is acid or alkaline, and this is especially the case where the water is just on the border-line between acidity and alkalinity.

The usual test for an acid is its sour taste and its power of causing effervescence with carbonates, but in the case of these waters the amount of acid may be so small that it does not reveal its presence by its taste, and if it causes any liberation of carbonic acid at all, the quantity liberated is so small that it remains dissolved in the water and its presence is not visible. Under these conditions it is necessary to seek the aid of a body which is peculiarly sensitive to the presence of an acid or an alkali, and which marks this sensitiveness by a distinct change in its colour. These bodies which are called indicators are in reality, so to speak, bodies put into the witness box to give their evidence as to the acidity or otherwise of the waters in question. As is the case with human witnesses, this evidence is not always reliable, for one indicator may say that the water is acid, another gives evidence to the contrary, and a third, whilst refusing to give direct evidence that the water is alkaline, will compromise matters by declaring that it is not acid. For instance, a weak solution of some organic acid gives no change of colour with Methyl Orange, but Lacmoid or Azolitmin may give distinct change of colour and declare it to be acid.

Phenolphthalein gives no change of colour with bicarbonate of soda, which is strongly alkaline salt and neutralizes strong mineral acids. The characteristic of phenolphthalein is to give a pink colour with alkalis, and unless this weakness on the part of phenolphthalein were known, it would immediately be assumed that the solution was not alkaline. Methyl Orange, which is yellow in colour, changing to pink with acids, retains its colour when added to an alkaline solution, so that the only evidence that methyl orange gives in this case is negative, and is that the water is not acid. Although under certain circumstances the evidence of these indicators may be unreliable, this does not mean that the true facts cannot be obtained by their instrumentality. It is known that the principal disturbing cause with phenolphthalein is carbonic acid, and if this disturbing cause can be removed, this indicator will give reliable results. In the case mentioned where phenolphthalein gives no pink

colour with bicarbonate of soda, if the solution be boiled the semi-combined carbonic acid will be expelled, and the remaining carbonate of soda will give the usual pink colour. With methyl orange again, if a water coloured yellow with this indicator is turned red by one drop of very dilute acid, then the water could not have been alkaline, since a very small quantity of acid causes the change of colour. If, however, a considerable quantity of acid is required to cause the change of colour, then there must be something in the water which is preventing the acid from acting on the methyl orange, and this can only be an alkali. If the quantity of water is measured and the strength of the acid known, the quantity used to effect the change of colour can be taken as a measure of the alkalinity of the water. By reversing the process and adding an alkali of known strength to a measured quantity of water shown to be acid by a suitable indicator, a measure of the quantity of acid can be obtained, and it is in this way that the amount of acid or alkali in a water is determined.

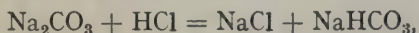
Discrimination must be taken in the selection of the most suitable indicator, and some knowledge of what the water is likely to contain should have been obtained before the indicator is selected. For instance, methyl orange should not be selected for a boiler water, as this indicator is particularly unreliable in the presence of nitrites, and most boiler waters contain nitrites.

When methyl orange is added to a water and does not turn pink, the only inference which can be correctly drawn is, that the water is not acid. It does not follow that it is alkaline, as methyl orange retains its colour both in neutral and alkaline solutions, and in this case the water may be quite neutral.

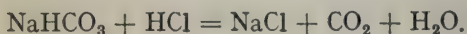
If phenolphthalein is added to a water and a red colour obtained, this not only shows that the water is not acid, but also that it is alkaline, but it does not show whether this alkalinity is due to carbonate of soda, caustic soda or free lime. The alkalinity may be due to any of these bodies or to a mixture. If, however, there is free lime there cannot at the same time be carbonate of soda, for the free lime would take away the carbonic acid from the soda and form carbonate of lime and caustic soda, and the pink colour would be caused by caustic soda. The mixture, however, might contain carbonate of soda and caustic soda, or free lime and caustic soda, as all these affect phenolphthalein.

If acid is gradually added to a solution of carbonate of soda coloured pink by phenolphthalein, a point is reached when the

colour is just discharged. At this point the liquid is therefore acid to phenolphthalein, but if methyl orange is then put into the same solution it remains yellow and is therefore not acid to methyl orange; and it remains yellow until as much more acid is added as was originally required to discharge the phthalein colour. This solution is therefore at one and the same time acid to phenolphthalein and alkaline to methyl orange. In this case double the amount of acid is required to render the solution acid to methyl orange as is required to make it acid to phenolphthalein. The explanation is this: when the acid is gradually added to a solution of carbonate of soda, the acid unites with the base soda and carbonic acid is set free. And as at this time the solution still contains some carbonate of soda, the liberated carbonic acid unites with it to form bicarbonate of soda, which has no action upon phenolphthalein. When there is no longer any carbonate of soda left to unite with this carbonic acid, the pink colour disappears and the solution only contains bicarbonate of soda. This point obviously occurs when half the carbonate of soda has been killed by acid, thus:—



and when more acid is added to the bicarbonate, the carbonic acid is all expelled and a neutral soda salt left. Any addition of acid beyond this point will then affect the colour of the methyl orange.



Therefore in taking the strength of carbonate of soda solutions, the amount of acid required to discharge the red phenolphthalein colour must be doubled when making the calculations, or methyl orange used as the indicator.

Alkalinity is, then, a somewhat elastic term and may mean little or much. Bicarbonate of lime is an alkaline salt and neutralizes acids. This alkalinity is a vanishing or temporary alkalinity, for on boiling the solution carbonic acid is expelled, carbonate of lime is precipitated, and the solution loses its power of destroying acids and is no longer alkaline. Free lime alkalinity is a restricted but true alkalinity. At ordinary temperatures lime alkalinity cannot exceed .125 per cent. or about 87.5 grains per gallon. This alkalinity rapidly decreases as the solution is heated, and at 212° F. it falls to .056 per cent. or 39.6 grains per gallon, and at the pressure and temperature of 200 lb. of steam

the alkalinity falls to about .007 per cent. or 5 grains per gallon. For this reason a boiler water can never attain a greater lime alkalinity than 5 or 6 grains per gallon, and when this alkalinity is reached any fresh addition of lime must come down as a lime scale.

Soda alkalinity, on the other hand, whether due to carbonate of soda or caustic soda, is a true alkalinity, and can accumulate to an extent very much greater than is ever likely to be obtained in boiler waters. Not only can it accumulate to the maximum solubility of carbonate of soda, but it can go further than this in boiler waters owing to the fact that at high pressures the carbonate is converted into caustic soda, the solubility of which in hot water is almost unlimited.

This alkalinity question can often be very misleading and cause much trouble. For instance, instructions to keep a certain feed water at 3° of alkalinity were given. On testing the water with Standard Acid and methyl orange as indicators, the water was found to be 3.0 of alkalinity, and it was assumed that the water was all right. In point of fact it was all wrong, for this alkalinity was due to bicarbonate of lime. On heating the water in the boilers this alkalinity vanishes and there is nothing left in the water to destroy the small amount of sulphate of lime; which the alkalinity was designed to destroy. In consequence a sulphate of lime scale was formed. The instructions should have been to give the water a carbonate of soda alkalinity of 3.0°, which would have been sufficient to have destroyed the small amount of sulphate of lime in the water.

For these reasons it would be better to regard bicarbonate of lime waters not as alkaline waters, but as waters having a temporary alkalinity, and confine the term alkaline to waters which owe their alkalinity to soda alone. This would prevent much confusion and prevent mistakes such as the one just recorded.

When a water has no marked acid or alkaline characteristics, it is sometimes very difficult to say on which side of the line of neutrality the water really lies. If the line MN in the accompanying diagram be taken to represent the line of neutrality, where the water is neither acid nor alkaline, the left-hand side of the line the acid line, and the right-hand side the alkaline, and the small circles various specimens of water, it is difficult in some cases to say on which side of the line the circle really lies.

There is no mistaking the positions of the circles marked 1-12; one lot is distinctly on the left side and the other on the right. But when they approach the line MN, the distinction is not so marked. So in practice it is often exceedingly doubtful on which side of the line of neutrality a water is to be placed, and as different indicators have different degrees of sensitiveness or delicacy, this difficulty is enhanced.

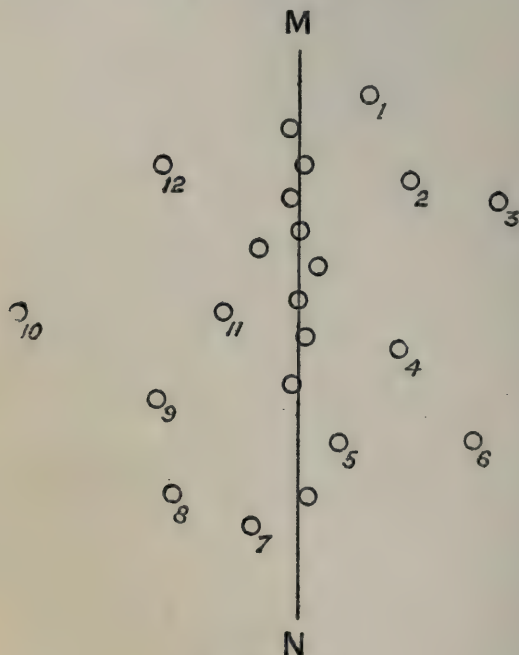


DIAGRAM 17.

Where very small quantities of acid or alkali have to be dealt with, the ordinary method of titration with methyl orange is useless as it introduces a \pm error of .25 grain of CO_2 per gallon, a quantity which in many cases is greater than the total CO_2 present in the water. An approximation might be made by deducting the amount of this error, but a method in which the correction is greater than the total amount found can hardly be considered an accurate method of determination.

When there is no doubt about the alkalinity of the water and it requires a considerable amount of acid to neutralize it, methyl orange can be used provided this correction is made. Even then

the change of colour from yellow to pink is not so distinct to some observers as to others, and this leads to discrepancies between the results obtained by different operators.

On the other hand, phenolphthalein, rosolic acid and lacmoid give very sharp and distinct changes when the disturbing influence of carbonic acid is removed. The following tests were carried out on a London tap-water: 250 c.c. required 12.2 c.c. N/10 acid to neutralize it, using methyl orange as indicator. This works out at 7.51 grains of combined carbonic acid per gallon; 250 c.c. of the same water, titrated back with phenolphthalein as indicator required 11.8 c.c. of the same acid. Rosolic acid and lacmoid gave the same result, and the change of colour was very marked and distinct in each case. This works out at 7.26 grains of combined carbonic acid per gallon or .25 grain less than when determined by methyl orange. If it be required to determine the carbonate of lime in this way, the difference is .56 grain, or rather over half a grain of carbonate of lime per gallon. Therefore for very delicate work such as the estimation of acid in condensed waters, methyl orange is not suitable.

Phenolphthalein only turns red in the presence of caustic soda, carbonate of soda, free lime or ammonia, and thus does not show whether a water is acid.

Lacmoid is often a useful indicator, giving a distinct red colour with acid, and a blue colour with alkali. In the presence of carbonic acid there is an intermediate stage where the colour is wine-red and this detracts from its value as an indicator. If, however, carbonic acid is not present or can be removed, both lacmoid and phenolphthalein can be made to give very accurate results.

A convenient method is as follows: measure out a convenient quantity of the water, say 250 c.c., add one or two drops of methyl orange and titrate with Standard Acid. When the water has been neutralized in this way, add a measured excess of the Standard Acid, say 5 c.c., and boil for five minutes to expel the carbonic acid. Then cool, add phenolphthalein, and titrate back with Standard Caustic Soda until a pink colour is just obtained. The amount of caustic soda solution required deducted from the total acid used, is the exact quantity required to neutralize the water. Lacmoid can also be used in this way, and the change of colour is much more marked and sudden than with methyl orange.

The Standard Acid used is preferably Nitric Acid, as it is not

volatile when heated, and does not expel its equivalent of hydrochloric acid from the chloride of sodium present in most waters. Sulphuric acid, on the other hand, although not volatile, expels both nitric acid and hydrochloric acid when boiled with nitrates and chlorides.

With very small quantities of acid or alkali, such as are found in rain-water and condensed water, Rosolic Acid is a very useful and delicate indicator. With a slight trace of alkali, whether due to carbonates, bicarbonates or caustic alkali, it gives a distinct pink colour and with acid a yellow colour.

Azolitmin is also a most delicate indicator, giving a red colour with acids and a blue colour with alkalies. The natural colour of Azolitmin is wine-red, and with exceedingly small quantities of acid it gives various shades of purple, claret and red. By matching these tints with solutions containing a known quantity of acid, and tinted with a measured quantity of Azolitmin solution, the quantity of acid can be determined colorimetrically. The alkalinity of very faintly alkaline solutions can also be determined in this way by matching the blue tints. The method is, however, troublesome and tedious and necessitates the use of special solutions.

CHAPTER III

CONSTITUENTS OF NATURAL WATERS

SILICA (SiO_2) is only soluble in water to the extent of .28 grain per gallon, and it is more than probable that the silica found in natural waters exists in the form of silicate of alumina and iron, derived from silicious rocks by direct solution. The soil over or through which the waters have to pass consists largely of silicate of alumina and iron, and some of it is bound to become dissolved.

Silica is found in much larger amount in alkaline soda-waters, but as silica is soluble in alkalies it exists in these waters as silicate of soda, often to the extent of 5 or 6 grains per gallon.

The hydrate of silica or silicic acid ($\text{SiO}_2 \cdot \text{H}_2\text{O}$), on the other hand, is much more soluble, and it is possible under certain conditions to obtain a solution containing as much as 10 per cent. of this material. This is the colloidal form of silica, and when such a solution is boiled or treated with certain salts, the silica is rendered insoluble and comes down as a precipitate.

Formerly filtration was a merely mechanical process to remove visible particles from the water, and yield a clear effluent, and the mere passage of the water through clean sand introduced very little silica into the water. Filtration is now a much more complicated process, and is no longer a mechanical but is a biochemical one. Filtration is no longer confined to the removal of matters visible to the eye, but has become a process to remove those invisible microscopic organisms which rightly or wrongly are credited with the spread of enteric diseases. The object of the Water Authorities is to keep down the spread of disease, and filtration has become a more elaborate process.

On the surface of the sand a film of harmless living organisms is developed. These organisms eat up and prey upon the harmful ones and so remove them from the water which is to be afterwards used for drinking purposes. Strictly speaking, this

is a biological process, but as the types of life undergoing transformation are lowly types, chemistry plays a conspicuous part in the operation, whereby harmful organic matters are converted into carbonic and nitric acids, and as oxygen is given off by the vegetable Saprophytes, the water is well aerated and becomes organically purified.

Amongst these Saprophytes are the diatoms, and as these exist in myriads they play an important part in the process of filtration. The diatoms consist of an outer skin of silica within which is contained a jelly-like mass, and this jelly has the power of assimilating silica to build up the skeletons, and to do this the jelly must have the power of rendering silica soluble, or in other words, of converting it into the colloidal or hydrated form. The upper layer of the sand filter is the material which furnishes that part of the food, which enables these diatoms to build up their skeletons, and enables them to continue their active digestion of the objectionable bacteria. These organisms in their turn die or are eaten up by other organisms and yield up the soluble silica to the water, and it is to this cause that many Town Supplies owe the greater part of their silica, certainly any amount over .28 grain per gallon.

These organisms are not always silicious but are often calcareous, and this seems to depend largely on temperature or, what is the same thing, the time of year, the silicious varieties being specially abundant in the winter time. Kieselguhr is a natural earth composed of the skeletons of silicious diatoms, and vast deposits of it are found scattered over the earth, and sometimes at the bottom of ponds. Divested of its impurities, which are generally alumina and carbonate of lime with more or less organic matter, it is nothing more than 80 per cent. silica and 20 per cent. of water of hydration, which is approximately $\text{SiO}_2 \cdot \text{H}_2\text{O}$.

Distilled water agitated for four hours with old weathered granite in a turbine stirrer, dissolved up silica to the extent of .28 grain per gallon. Tap-water containing .95 grains of silica per gallon, when treated in the same way did not dissolve any more silica.

A hydrate of silica, which had been dried on the water-bath and contained 13.2 per cent. of water of hydration, when similarly treated with distilled water, went into solution to the extent of 4.48 grains per gallon. The approximate constitution of this hydrate was $2\text{SiO}_2 \cdot \text{H}_2\text{O}$.

ALUMINA AND OXIDE OF IRON

Small quantities of these bodies are always found in natural waters. The amount seldom reaches .20 grain per gallon, and is generally about .10 grain. The amount recorded in water analyses is principally alumina, the amount of the oxide of iron being seldom more than one-tenth of the alumina, in fact oxide of iron is so insoluble in water as to be considered negligible.

Ferrous oxide, on the other hand, is soluble in water to the extent of .50 grain per gallon, but as it rapidly takes up oxygen and becomes converted into ferric oxide, it would come out of solution. When any appreciable amount of ferrous oxide is found in a natural water it generally exists as bicarbonate, and even then it is soon deposited by exposing the water to the air.

CARBONATE OF LIME

Carbonate of lime is only very slightly soluble in water alone, and only goes into solution in any appreciable quantity by the aid of carbonic acid, with which it forms a more or less soluble bicarbonate $\text{CaH}_2(\text{CO}_3)_2$ or $\text{CaCO}_3 \cdot \text{H}_2\text{CO}_3$. If carbonic acid be looked upon in the light of a true acid, then the view may be taken that carbonate of lime is not soluble in water, but is soluble in carbonic acid in the same way as it is in other acids. There is this difference, however, that the carbonic acid is not expelled from the carbonate of lime but remains in the new combination. On the other hand, when an acid such as sulphuric acid is used, the carbonic acid is expelled and a new salt is formed containing no carbonic acid. Hence when the latter solution is boiled, no carbonate of lime can be deposited. When the solution of carbonate of lime in carbonic acid is boiled, the carbonic acid which has been used to dissolve it is driven off, and the carbonate of lime being insoluble in water, can be recovered in its original form.

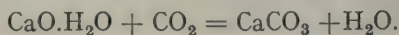
Carbonate of lime exists in Nature in the crystalline form as marble and limestone, and in a more or less amorphous state in the form of chalk and is very widely distributed. When heated to a temperature approaching a red heat it is resolved into its constituents, lime and carbonic acid, the latter coming off as gas and leaving quicklime or caustic lime (CaO).

The temperature at which the carbonate is decomposed is considerably lowered if a current of air or steam is passed over

the heated mass. Lime in the form of hydrate is also formed by heating the carbonate in a current of superheated steam at a much lower temperature than a red heat, and calcium hydrate formed in this way is frequently found in superheaters where carbonate of lime sludge has been carried by the steam from the boilers.

When quicklime is carefully sprinkled with water, a part of the water is absorbed, considerable heat is evolved and the quicklime falls to a fine dry powder known as slaked lime or calcium hydrate. This calcium hydrate is soluble in water, and before quicklime can go into solution in water it must become hydrated.

When a stream of carbonic acid gas is passed into a saturated solution of calcium hydrate, carbonate of lime is first precipitated, according to the following equation:—



When the whole of the lime is thus precipitated, the carbonic acid begins to redissolve it, forming bicarbonate of lime, and continues to do so until the water is saturated with bicarbonate of lime, thus:



As the point of saturation for bicarbonate of lime is reached before the whole of the precipitated carbonate of lime is redissolved, the solution can never become quite clear again, that is to say, there is always a residual precipitate. Put into other words, the solubility of bicarbonate of lime is relatively less than that of free lime.

The following experiment was made to illustrate this. A stream of carbonic acid was passed into water saturated with lime at 65° F. for four hours. The precipitate first formed was partially but not entirely dissolved. The filtered liquid contained 63·80 grains of carbonate of lime, which is equivalent to 103·36 grains of bicarbonate of lime per gallon. As the liquid contained 84·2 grains of carbonic acid over and above that required to form the bicarbonate, and there was still an excess of undissolved carbonate of lime, this point should mark the maximum solubility of bicarbonate of lime at 65° F.

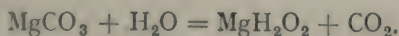
The 103·36 grains of bicarbonate of lime are equivalent to 35·73 grains of lime (CaO), and as the original lime-water contained 85·60 grains of free lime, the solubility of bicarbonate of lime is relatively much less than that of free lime.

The solubility of bicarbonate of lime was confirmed in another way. Equivalent quantities of nitrate of lime and bicarbonate of soda were mixed together at 65° F., considerably diluted and allowed to stand for four hours. A large amount of crystalline precipitate was formed and the clear filtered liquid contained 63.4 grains of carbonate of lime per gallon, which is equivalent to 102.87 grains of bicarbonate of lime. This result is in very close agreement with the figure obtained by passing carbonic acid into lime-water, and it may therefore be taken that the maximum solubility of bicarbonate of lime at 65° F. is 103 grains per gallon.

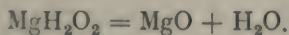
If all the lime contained in a saturated solution of lime-water could be fully converted into bicarbonate of lime, it would yield 247.7 grains of bicarbonate, but as the solubility as shown above only amounts to 103 grains, the whole of the lime in saturated lime-water can never be redissolved by a stream of carbonic acid, and there must always be a residual precipitate, however long the stream of carbonic acid is continued.

CARBONATE OF MAGNESIUM

Carbonate of Magnesium exists in natural waters in the form of bicarbonate ($\text{MgH}_2(\text{CO}_3)_2$). When its solution is boiled it is resolved into carbonate of magnesia which is precipitated and carbonic acid gas which is expelled. When the heating takes place in boilers, the carbonate of magnesia undergoes a further transformation and is gradually resolved into Magnesium Hydrate and carbonic acid.



And in cases where the boiler pressure is high the magnesium-hydrate loses its water of hydration and is converted into magnesium oxide.



Precipitated magnesium hydrate is very light and tends to rise to the surface of the water in the boilers, and if from any cause frothing or priming takes place, it is caught up with the rush of steam and finds its way into the steam pipes and engines. Carbonate of lime will also do this, but generally only when the boiler water becomes very dense.

Magnesium hydrate so precipitated, especially when deposited from dense boiler waters, has often a very beautiful appearance

resembling aluminium paint. These silvery spangles have the same composition as the natural mineral known as Brucite ($\text{MgO} \cdot \text{H}_2\text{O}$).

The solubility of carbonate of magnesia in water *per se* is very much greater than that of carbonate of lime. The hydrate of magnesia is, however, very slightly soluble, and in this respect differs from the hydrate of lime.

CARBONATE OF SODA

Carbonate of Soda (Na_2CO_3) is an alkaline salt very soluble in water and much used for precipitating lime from water, where the lime exists in any form but the carbonate. Carbonate of lime being insoluble, a precipitate is obtained when carbonate of soda is added to a solution containing lime in the form of nitrate, sulphate or chloride.

Solubilities of Carbonate of Soda

<i>Temperature.</i>	<i>Parts per 100.</i>
32° F.	7.08
40° F.	16.66
68° F.	25.93
77° F.	30.83
96° F.	35.90
221° F.	48.50

It melts at about 1400° F. with little or no decomposition, but at higher temperatures a little carbonic acid is given off and some caustic soda is formed. Superheated steam also decomposes it into carbonic acid and caustic soda.

Where a solution of carbonate of soda is evaporated at pressures greater than 100 lb. per sq. inch, caustic soda is formed. The reaction is not a mere separation of the carbonic acid and the soda, for oxygen is given off at the same time and formate of soda (NaCHO_2) and other degraded forms of carbonic acid are found in solution. The formate of soda in its turn is decomposed into formaldehyde (CH_2O), which by a process of polymerization is condensed into a sugary body such as formose ($\text{C}_6\text{H}_{12}\text{O}_6$). This sugar or carbohydrate by continued boiling with the rapidly concentrating caustic soda, causes other reactions, whereby acetone lactic acid and perhaps hydrocarbons are driven off and a portion of the caustic soda reconverted into carbonate of soda. The volatile matters pass off with the steam. Steam from high-

pressure boilers is generally acid and causes considerable corrosion in the feed pipes and economizers when the condensed steam is used as a boiler feed. It is somewhat remarkable that condensed waters from high-pressure boilers seldom if ever contain more than a trace of carbonic acid though they are always nearly saturated with free oxygen. The reactions which take place are exceedingly complicated and are often reversible, and the character of a boiler water evaporating a carbonate of soda water varies from day to day, some days showing unmistakable evidence of sugars, on other days of formic acid; whilst the ratio of the caustic soda to the carbonate of soda seems to be continually changing. The practical application of these reactions will be further dealt with in the chapter on Carbonic Acid.

Strength of Carbonate of Soda Solutions

Spec. Gravity at 60° F.	Baume Degrees.	Weight per cent. Na ₂ CO ₃ .
1·007	1	0·67
1·014	2	1·33
1·022	3	2·09
1·029	4	2·76
1·036	5	3·43
1·045	6	4·29
1·052	7	4·94
1·060	8	5·71
1·067	9	6·37
1·075	10	7·12
1·083	11	7·88
1·091	12	8·62
1·100	13	9·43
1·108	14	10·19
1·116	15	10·95
1·125	16	11·81
1·134	17	12·43
1·142	18	13·16
1·152	19	14·24

SULPHATE OF LIME

Sulphate of Lime (CaSO₄) is found native as anhydrite (CaSO₄), and in the hydrated form (CaSO₄·2H₂O) as selenite, gypsum, alabaster, etc. It also occurs in a sea-water to a considerable extent, and is a constituent of most natural waters.

The anhydrous sulphate is not soluble in water, but it readily takes up water to form the hydrate (CaSO₄·2H₂O), and it is this hydrate which dissolves in water. Plaster-of-Paris is a hydrate containing less water than gypsum, and has the property of taking up water and setting to a hard mass.

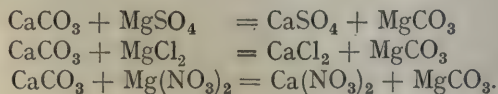
The following table gives the solubilities at various temperatures :—

<i>Temperatures.</i>	<i>CaSO₄ in grains per gallon.</i>
32° F.	133·0
68° F.	144·2
106° F.	149·8
140° F.	145·6
176° F.	136·5
212° F.	121·8

From this it appears that the solubility increases from 32° F. to about 100° and then falls and becomes less soluble in boiling water than it is at 32°. When a water containing sulphate of lime is heated in a boiler to a temperature of about 260° F. the hydrated sulphate loses its water of hydration, becomes converted into the anhydrous sulphate (anhydrite), which being insoluble is deposited as a hard crystalline scale. Thus both the sulphate and carbonate of lime are deposited by a process of chemical decomposition, the sulphate because the temperature of the water compels it to part with its water of hydration, the carbonate because its solvent carbonic acid is expelled.

Sulphate of lime is found in some natural waters in quantities greater than the solubilities given above, and is evidently more soluble in certain saline solutions than it is in pure water. This may also account for the fact that sulphate of lime is frequently found in boiler waters containing chloride of sodium, although the water has been heated for a considerable period of time above the temperature at which the sulphate is dehydrated. It may, however, be due to a double decomposition by which chloride of calcium and sulphate of sodium are formed, still the fact remains that some of the lime remains in solution and is not precipitated as an insoluble sulphate.

There is also a secondary reaction whereby magnesia is deposited, although it may exist in the water either as sulphate chloride or nitrate, which are all soluble salts. In this case the carbonate of lime reacts with these salts, forming carbonate of magnesia and the corresponding lime salt. Thus :—



The precipitated carbonate of magnesia further undergoes decomposition, yielding magnesia.

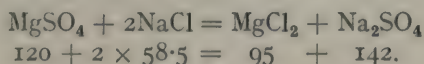
In the case of the sulphate, the sulphate of lime comes down as scale, and it is thus not infrequent to find a sulphate of lime scale where the original water contains no sulphate of lime.

Calcium chloride is often found in boiler waters, and is produced in this way. Thus boiler waters into which sea-water has found its way always contain some chloride of calcium, although sea-water contains none. It is formed, as above stated, by the interaction of magnesium chloride and carbonate of lime, and the action also explains why there is insoluble magnesia in these boiler waters, although there is no carbonate of magnesia in sea-water.

This reaction between carbonate of lime and the soluble magnesia salts is of some importance not only from the boiler-water point of view, but also from the steam point of view, for the liberated carbonic acid may be carried away with the steam and cause the condensed water to become corrosive. As sea-water often contains as much as 10 grains of carbonate of lime per gallon, this together with the free carbonic acid would furnish approximately 8.8 grains of carbonic acid per gallon, which is equivalent to $1\frac{1}{4}$ lb. of carbonic acid from each 1,000 gallons of sea-water.

SULPHATE OF MAGNESIA

Sulphate of Magnesia (MgSO_4) is very soluble both in hot and cold water, and does not play any important part in Boiler Chemistry except for its reactions with other salts in the water such as carbonate of lime and chloride of sodium. In the former case it can yield insoluble sulphate of lime, and in the latter case it is a potential source of chloride of magnesium, thus :—



so that every 120 parts of sulphate of magnesium is the potential source of 95 parts of chloride of magnesium, and each grain of sulphate of magnesium when brought into combination with chloride of sodium can yield .80 grains of chloride of magnesium, that is, four-fifths of its weight.

SULPHATE OF SODIUM

Sulphate of Sodium (Na_2SO_4) is under ordinary conditions a very soluble inert salt. It occurs in many waters and in mineral

springs, and is occasionally found native as Thenardite; in conjunction with sulphate of lime as Glauberite ($\text{Na}_2\text{SO}_4\text{CaSO}_4$), and with sulphate of magnesia as Loweite ($\text{Na}_2\text{SO}_4\text{MgSO}_4$).

It melts at about 1600°F. , and when heated with carbon out of contact with air it is reduced to sulphide of sodium (Na_2S). It is also reduced at a red heat by hydrogen and carbon monoxide, whereby caustic soda is formed, in addition to sulphide of sodium and some sulphuretted hydrogen (H_2S) given off. When heated with silica, the silica expels the sulphuric acid and silicate of soda is formed. When sulphate of soda is heated with metallic iron, ferric oxide, ferrous sulphide, sodium sulphide and sodium oxide are formed. By melting sulphate of soda in a thin iron capsule, the iron is rapidly corroded and the melted mixture perforates the crucible.

Sulphate of soda is more soluble in cold than in hot water. The maximum solubility occurs at about 65°F. , from which point to boiling point the solubility steadily diminishes, as can be seen from the accompanying diagram, which also gives the solubilities of chloride, nitrate and carbonate of sodium. The latter has a rising solubility as the temperature increases and the two curves approach each other.

Solubilities of Sulphate of Soda

<i>Temperature.</i>	<i>Parts per 100.</i>
65°F.	53.25
68°F.	52.76
77°F.	51.53
79°F.	51.31
86°F.	50.37
91°F.	49.71
93°F.	49.53
104°F.	48.78
113°F.	47.81
122°F.	46.82
140°F.	45.42
158°F.	44.35
185°F.	42.96
218°F.	42.65

Sulphate of sodium combines with sulphuric acid to form bisulphate of soda, commonly called the acid sulphate (NaHSO_4). Bisulphate of soda is a tough white mass very soluble in water. At 400°F. it melts, giving off sulphuric acid and leaving a residue of the ordinary or normal sulphate.

A solution of bisulphate of sodium is strongly acid, and for many purposes can be used in the place of sulphuric acid. A

crude form of bisulphate of soda is known as saltcake, and is now largely used to replace sulphuric acid, which is at present very scarce and often unobtainable. Nitre cake is another

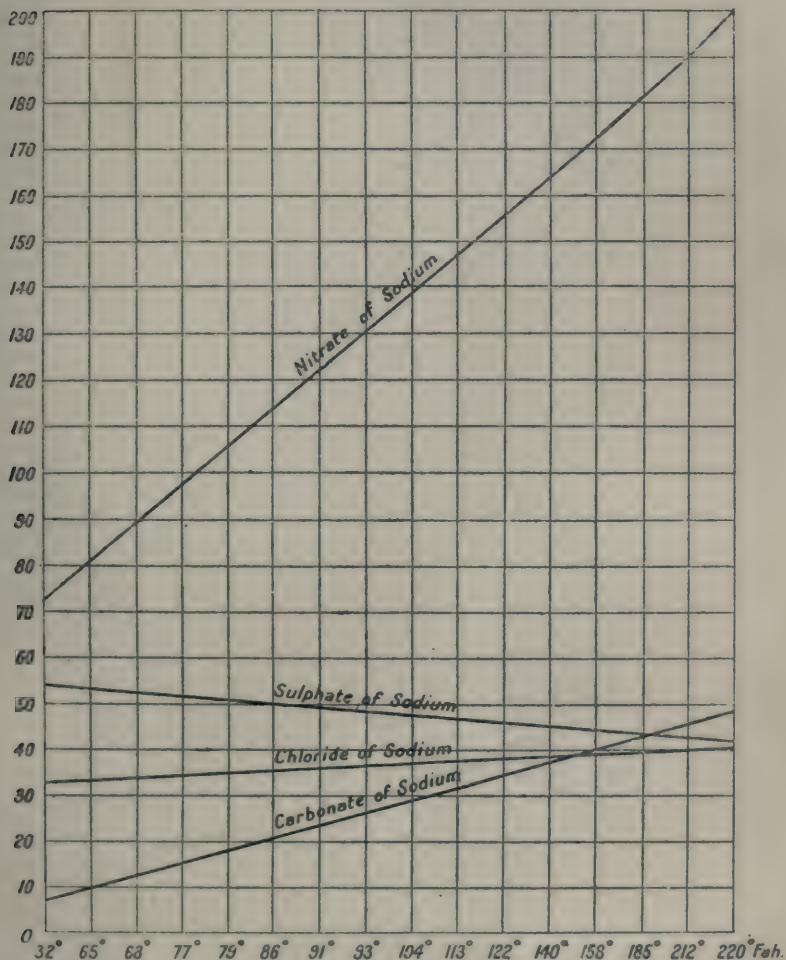


DIAGRAM 18.

form in which bisulphate is obtainable. In this case it is the residue from the manufacture of nitric acid, whilst saltcake is obtained in the manufacture of hydrochloric acids. As the whole of the nitrate or chloride of sodium in these cakes has

not been decomposed, the solution obtained by dissolving them up in water contains nitric or hydrochloric acid in addition to the sulphuric.

Bisulphate of soda rapidly attacks iron, either in solution or when melted, the product being a mixture of ferrous and ferric sulphates.

NITRATE OF LIME

Nitrate of Lime ($\text{Ca}(\text{NO}_3)_2$) is an exceedingly soluble salt, generally present in soils and in many natural waters. It is soluble in water to an almost unlimited extent.

The dry salt melts at 1040°F. , giving off oxygen and nitric oxide and leaving a residue of lime. When its solution is evaporated in high-pressure boilers it is partially decomposed, the solution becomes alkaline owing to the separation of free lime and some nitrite of lime is formed. Most boiler waters containing nitrate of lime also contain nitrites formed in this way. The salt is corrosive and attacks iron, with the formation of ferric oxide and nitrite of lime.

Nitrate of lime is a powerful oxidizing agent and somewhat readily parts with its oxygen, so that organic matters in the water can also cause the formation of nitrites and possibly also further reduce the nitrites to ammonia, which would escape with the steam and leave the lime in the form of carbonate of lime or calcium hydrate, in the latter case rendering the water slightly alkaline. Such an alkalinity is often found in boiler waters and is often mistaken for a soda alkalinity. For the reason that such a boiler water gives a pink colour to phenolphthalein, it is too often assumed that the boiler water is in good condition, whereas it is really corrosive owing to the fact that this slight alkalinity, which can never exceed 5 or 6 grains per gallon at boiler temperatures, is not sufficient to protect the iron from corrosion.

NITRATE OF MAGNESIUM

Nitrate of Magnesium ($\text{Mg}(\text{NO}_3)_2$) is also a very soluble salt, in all respects analogous to nitrate of lime. As, however, any magnesia which is liberated by its decomposition is practically insoluble, the water does not become alkaline as it does with nitrate of lime.

When nitrate of magnesia is boiled with carbonate of lime,

nitrate of lime is formed together with carbonate of magnesia which in its turn breaks up into magnesia and carbonic acid.

NITRATE OF SODIUM

Nitrate of Sodium (NaNO_3) is also a very soluble salt more soluble in hot water than in cold water, so that the solubility rises with the temperature up to the boiling point.

The dry salt melts at 600°F. and is decomposed, being first transformed into nitrite of soda and finally into sodium oxide. It easily parts with its oxygen, and when heated to the melting point with metallic iron converts it into magnetic oxide and leaves sodium oxide.

In solution it is readily reduced by organic matter, nitrites being formed and carbonic acid and ammonia are given off.

Solubilities of Nitrate of Soda

<i>Temperature.</i>	<i>Parts per 100.</i>
32°F.	72.9
50°F.	80.8
68°F.	87.5
96°F.	94.9
104°F.	102.0
122°F.	112.0
140°F.	122.0
158°F.	134.0
176°F.	148.0
194°F.	162.0
212°F.	180.0
220°F.	200.0

CALCIUM CHLORIDE

Calcium Chloride (CaCl_2) is an exceedingly soluble salt seldom found in natural waters, but often found in boiler waters evaporating sea-water or waters containing carbonate of lime and chloride of magnesium. It is so soluble that water will dissolve more than its own weight of this salt.

MAGNESIUM CHLORIDE

Magnesium Chloride (MgCl_2) is a very soluble salt frequently found in natural waters. In dilute solution it has a very corrosive action upon iron, hydrogen being given off and the iron converted into ferrous oxide which does not go into solution. The reaction appears to be catalytic as the chloride of magnesium

undergoes no diminution, and no magnesia comes out of solution. The water is alone decomposed, its oxygen going to the iron and the hydrogen liberated as gas.

SODIUM CHLORIDE

Sodium Chloride (NaCl) occurs in all waters and is especially abundant in sea-water. It melts without decomposition at about 1400°F . and is partly volatilized at a white heat. In solution it is inert and does not of itself cause corrosion. In conjunction, however, with sulphate of magnesia it becomes very corrosive. Iron sealed up in a solution containing chloride of sodium and sulphate of magnesia evolves hydrogen and is converted into ferrous oxide, so that although sodium chloride is not of itself active it is potentially active if there is any sulphate of magnesia in the water.

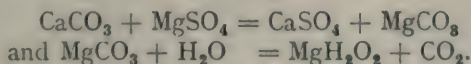
Solubilities of Sodium Chloride

<i>Tempera- ture.</i>						<i>Parts per 100.</i>
32°F.	35.52
43°F.	35.62
48°F.	35.74
57°F.	35.87
77°F.	36.13
94°F.	36.64
122°F.	36.98
140°F.	37.25
158°F.	37.88
176°F.	38.22
194°F.	38.87
212°F.	39.61
220°F.	40.35

CHAPTER IV

SCALES AND DEPOSITS

WHEN water is heated in the boiler, steam and gases are driven off and the boiler water contains all the solid impurities in some shape or form. Some of these become insoluble and form an incrustation or scale which adheres to the heating surfaces, or a sludge may be formed which remains in suspension in the boiler water. Other impurities, on the other hand, remain in solution, and sooner or later form such a concentrated solution that it has to be got rid of by emptying the boiler. Secondary reactions between the sludge and the salts remaining in solution often take place and form deposits or scale of another character. For example, when the water contains carbonate of lime and nitrate of magnesia, the carbonate of lime first comes down partly as a hard scale and partly as a sludge. By continued boiling the carbonate of lime reacts with magnesium nitrate, forming carbonate of magnesia and nitrate of lime. Nitrate of lime is a very soluble salt and remains in solution, whilst the carbonate of magnesia, being insoluble, comes out of solution and is resolved by further boiling into magnesium hydrate and carbonic acid. In this way magnesia which exists in a water in a permanently soluble form is frequently precipitated, and it is not at all an uncommon occurrence to find that waters containing nitrate, chloride or sulphate of magnesia lose this magnesia when heated in high-pressure boilers. In this way it is often possible to get a sulphate of lime scale in a boiler, although the feed water contains no sulphate of lime. The reaction is expressed by the equation :—



The amount of scale that would be formed in a boiler evaporating water containing 10 grains per gallon of carbonate of lime,

at the rate of 1000 gallons per hour for 1000 hours, would be 10,000,000 grains or 1430 lb. This quantity would very seriously interfere with the efficiency of the boiler and cause much trouble.

SCALES

The carbonate of lime is first deposited in the amorphous form, as it is when precipitated from solution in the cold. This amorphous precipitate gradually becomes converted into the crystalline form (Calcite), at the same time shrinking in bulk and becoming denser, and forms a sludge instead of a hard adhering scale. As the deposition is very gradual, a portion of the carbonate is not deposited in this form, but slowly comes down in the crystalline state (arragonite), and it is this part of the carbonate of lime which forms the adherent scale. Only a part of the carbonate of lime forms scale, the remainder coming down as a sludge, and this sludge is sometimes carried up with the steam into the steam pipes and engines.

Sulphate of lime, on the other hand, is all deposited in the crystalline state. As it undergoes no further change by continued boiling it accumulates by further aggregation into a hard, compact, solid, non-porous scale. As the carbonate of lime is still depositing, some of this is deposited on the sulphate or the sulphate on the carbonate, and the scale becomes a mixture of carbonate and sulphate of lime when both salts exist together in the water.

Magnesia, which is first deposited as carbonate, shrinks as it gradually becomes converted into hydrate or oxide, and does not usually form a scale. It is generally found in much smaller quantities than either the sulphate or carbonate of lime, and enters into the composition of the scale by being imprisoned in the crystallizing magma, especially with scales containing sulphate of lime as the dominant constituent. This is more particularly the case with scales formed from waters which have only been partially softened. In the process of water softening it is always more easy to remove the carbonate of lime than the other constituents, and if a water has not been properly treated the residual hardness consists of sulphate of lime with more or less magnesia. The scale in this case consists of sulphate of lime with a good deal of magnesia, which has become entangled in the crystalline sulphate of lime.

EXAMPLES

The following water was used for feeding the boilers :—

Feed Water

Silica	•11
Oxide of Iron	•10
Sulphate of Lime	2•77
Carbonate of Lime	•91
Carbonate of Magnesia	•88
Chloride of Sodium	2•46
	<hr/>
	7•23
	<hr/>
Hardness	4•00°

The result of using this water was the formation of a very considerable quantity of both scale and sludge.

Scale from Front of Boiler

Silica	2•28
Oxide of Iron	2•00
Sulphate of Lime	75•38
Carbonate of Lime	13•28
Magnesium Hydrate	6•09
Organic Matter, etc.	•97
	<hr/>
	100•00
	<hr/>

Scale from Back of Boiler

Silica	7•08
Oxide of Iron	5•52
Sulphate of Lime	30•63
Carbonate of Lime	41•55
Magnesium Hydrate	10•64
Organic Matter, etc.	4•58
	<hr/>
	100•00
	<hr/>

Sludge

Silica	7•70
Oxide of Iron	5•12
Sulphate of Lime	27•25
Carbonate of Lime	46•09
Magnesium Hydrate	10•48
Organic Matter, etc.	3•36
	<hr/>
	100•00
	<hr/>

The sludge and the scale deposited on the back or cooler part of the boiler consists chiefly of carbonate of lime, while the scale

from the front or hottest part consists principally of sulphate of lime. These three samples were all taken from the same boiler.

Carbonate of lime scales, although troublesome and detrimental to the efficiency of the boilers and therefore to be avoided, are not nearly so destructive as sulphate and silicate scales. The carbonate scales are to a certain extent porous, and allow penetration of the boiler water and are also comparatively easy to remove. As a rule the carbonate scales are contaminated with magnesia and more or less sulphate of lime, but occasionally they are comparatively pure carbonate of lime, the percentage of which sometimes rises well into the nineties. The following are typical examples of purely carbonate scales:—

Carbonate Scales

Carbonate of Lime	94.90
Magnesium Hydrate	1.57
Oil	3.53

100.00

Carbonate of Lime	91.52
Sulphate of Lime	3.67
Magnesium Hydrate	1.57
Chloride of Sodium18
Moisture	2.76

99.70

Silica	5.30
Alumina, etc.	3.40
Carbonate of Lime	81.21
Magnesium Hydrate	8.67
Organic Matter, etc.	1.42

100.00

Silica	1.90
Carbonate of Lime	93.15
Phosphate of Lime81
Carbonate of Magnesia	4.14

100.00

The first three samples are scales taken from the boiler itself, the last one from the feed pipes, hence the presence of carbonate of magnesia. As a rule the percentage of carbonate of lime is not nearly so high as in the examples given and may fall as low

as 50 per cent., below this percentage the dominant constituent may be sulphate of lime or magnesia. In this case the scale should be considered a sulphate of lime scale or even a magnesia scale.

The following scale, although it contains some carbonate of lime, could hardly be described as a carbonate scale. As it contains nearly as much hydrate of magnesia as sulphate of lime, it would hardly be correct to describe it either as a sulphate scale or as a magnesia scale.

Silica	3.08
Oxide of Iron	1.84
Carbonate of Lime	2.73
Sulphate of Lime	48.93
Magnesium Hydrate	42.18
Organic Matter, etc.	1.24
	<hr/>
	100.00
	<hr/>

Carbonate of magnesia is also precipitated from waters containing bicarbonate of magnesia and the precipitated carbonate is resolved into hydrate by further boiling. This magnesium hydrate is very light and tends to rise to the surface of the water in the boiler drums, especially if the boiler water gets very dense, and if from any cause priming or frothing takes place the hydrate is caught up with the rush of steam and finds its way into the steam pipes and engines. The efficiency of turbines is not infrequently reduced in this way, by the magnesia sludge clogging the blades or ports. Carbonate of lime sludge sometimes acts in the same way.

The following is an example of such a deposit found in steam pipes and also in the turbines:—

Silica	11.00
Alumina	26.16
Carbonate of Lime	2.00
Magnesium Hydrate	35.62
Organic Matter	16.12
Oil	9.10
	<hr/>
	100.00
	<hr/>

The frothing in this case was due to soap in the boiler water. The oil had not been completely removed from the feed water, and the organic matter found in the deposit is partially carbonized oil.

Although magnesia generally forms a fine floury deposit or sludge, sometimes it is found as a hard scale.

Magnesia Scale

Silica	·86
Oxide of Iron	·40
Sulphate of Lime	12·61
Carbonate of Lime	1·52
Magnesium Hydrate	78·64
Organic Matter, etc.	5·97
	<hr/>
	100·00
	<hr/>

Sometimes hydrate of magnesia is precipitated in a very beautiful form resembling silver spangles, and has been mistaken for aluminium paint, which it closely resembles. Analyses, however, shows it to be artificial Brucite (MgH_2O_2). The following is an analysis of a sample taken from a boiler where it had been deposited as a sludge:—

Artificial Brucite

Magnesium Hydrate	87·38
Silica	8·31
Alumina and Oxide of Iron	4·31
	<hr/>
	100·00
	<hr/>

The sample was dried before analysis, in the wet state it contained 39·13 per cent. of water over and above the water of hydration. When dried it still preserved its silvery appearance. This form of magnesia is only deposited from very dense boiler waters containing large quantities of magnesia and soda salts. The particular boiler water from which this sample was taken contained the following:—

Boiler Water

Sulphate of Lime	90·10
Sulphate of Magnesia	445·95
Magnesium Hydrate	10·96
Carbonate of Magnesia	32·28
Nitrate of Sodium	89·25
Sulphate of Sodium	10951·75
Chloride of Sodium	2211·30
	<hr/>
	13831·59
	<hr/>

The following is another example of a hard magnesia scale. In this sample it is cemented together by some sulphate of lime and

some oxide of manganese. It was taken from a boiler evaporating a colliery water which contained a small quantity of carbonate of manganese.

Magnesia Scale

Silica	2.08
Oxide of Iron	1.44
Oxide of Manganese	15.70
Sulphate of Lime	22.00
Magnesium Hydrate	58.71
	<hr/>
	99.93
	<hr/>

Sulphate of Lime also forms a scale in the boiler, but unlike the carbonate it is seldom found in a sludge, and even then only entangled with carbonate of lime and hydrate of magnesia sludge. Both the carbonate of lime and the sulphate of lime are deposited by a process of decomposition, the carbonate becoming insoluble because its solvent carbonic acid is expelled, the sulphate because at the temperature of the boiler water it has to part with its water of hydration. Sulphate of lime in scales from high-pressure boilers is always found as anhydrite (CaSO_4) and never as Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). The following analyses give two sulphate of lime scales. One is the scale from the inside of the boiler, and the other from the outside of the condensing towers where the water was used for cooling.

Sulphate Boiler Scale

Sulphate of Lime	94.62
Magnesium Oxide	4.20
Silica32
Oxide of Iron24
	<hr/>
	99.38
	<hr/>

Sulphate Condenser Scale

Silica	2.10
Oxide of Iron	3.14
Sulphate of Lime	68.10
Carbonate of Lime	8.07
Water of Hydration	18.03
	<hr/>
	99.44
	<hr/>

In the boiler scale the sulphate of lime exists as anhydrite (CaSO_4) and in the condenser scale as Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). The amount of gypsum in the above scale is therefore 86.13 per cent. ($68.10 + 18.03$). The anhydrite is deposited from the

boiler water by becoming dehydrated, and the gypsum from the condenser water because the point of saturation has been exceeded and being no longer soluble it is deposited in the hydrated state.

The following are other examples of sulphate of lime scales :—

Sulphate of Lime	98.89
Magnesium Oxide	1.05
		<hr/>
		99.94
		<hr/>

Silicate of Lime	3.19
Sulphate of Lime	88.59
Magnesium Hydrate	8.41
		<hr/>
		100.19
		<hr/>

Silica77
Oxide of Iron	3.20
Sulphate of Lime	91.41
Carbonate of Lime	2.07
Magnesium Hydrate	1.22
Organic Matter, etc.	1.33
		<hr/>
		100.00
		<hr/>

Silica22
Oxide of Iron09
Sulphate of Lime	96.88
Carbonate of Lime	1.23
Magnesium Oxide	1.58
		<hr/>
		100.00
		<hr/>

Silica08
Sulphate of Lime	95.62
Calcium Hydrate70
Magnesium Oxide	3.40
		<hr/>
		99.80
		<hr/>

The boiler water from which this scale was deposited contained :—

Boiler Water

Calcium Hydrate	4.66
Sulphate of Lime	37.25
Nitrate of Lime	362.73
Nitrate of Sodium	311.73
Chloride of Sodium	450.45
		<hr/>
		1166.82
		<hr/>

There was also a pearly deposit of shining scales of magnesium hydrate in the form of Brucite (MgH_2O_2).

Sludge

Magnesium Hydrate	91.16
Silicate of Magnesia	7.95
Moisture, etc.89
							<hr/>
							100.00
							<hr/>

In this case most of the magnesia came down as sludge, whilst the sulphate of lime formed a very hard scale difficult to remove. And as a general rule, although some magnesia may be found in the scale, the bulk of it comes down as sludge. The following is another typical instance, and both samples are taken from the same boiler :—

Scale

Silica31
Oxide of Iron	4.70
Sulphate of Lime	87.25
Magnesium Oxide	7.73
							<hr/>
							99.99
							<hr/>

Sludge

Silica	8.13
Oxide of Iron	7.08
Sulphate of Lime	5.05
Carbonate of Lime	32.79
Magnesium Hydrate	41.47
Organic Matter, etc..	5.25
							<hr/>
							99.77
							<hr/>

Sulphate scales are much harder than carbonate scales, they are non-porous and difficult to remove. For these reasons they prevent the proper transmission of the heat through the tubes and other heating surfaces to the water, the consequence being that the tubes and plates become unduly heated and strained, and often attain such a temperature that the external deposits formed from the fuel in the furnace become fused and attack the metal, causing blisters and bulges.

Silicate scales are even worse in this respect than sulphate scales, but such scales are not frequent, and when found are generally due to improper treatment of the water. Alkaline soda-waters dissolve silica somewhat freely, forming silicate of

soda, and when this silicate of soda is boiled with a lime salt, an insoluble silicate of lime is precipitated and forms a very hard non-permeable and destructive scale. Silicate of magnesia forms a similar scale, and these scales, though often very thin, adhere so firmly to the iron that they are much more destructive than much thicker incrustations of sulphate and carbonate of lime. Silicate scales are also caused by the use of bad lime in treating the water.

All chalks and limestones contain a considerable percentage of silica, and when these materials are burnt into lime, the silica remains in the lime. When the lime is mixed with soda ash and water, caustic soda is formed, and this caustic soda dissolves up a considerable quantity of silica to form silicate of soda, which goes forward with the water into the boilers. So long as the water contains no lime, no evil results, but there is sure to be a time when the whole of the lime is not removed from the water and some hard water gets into the boilers. The result is the formation of a silicate of lime or magnesia, and the tubes very soon fail. A silicate scale $\frac{1}{16}$ inch thick will cause tubes to fail in a few days. The silicate scales can be easily recognized by their enamel-like appearance. They are generally quite white and non-crystalline, whereas sulphate scales are generally highly crystalline. Sometimes they are associated with oxide of iron, in layers quite distinct from the white scale itself, thus showing that corrosion is also going on.

The following is an example of a silicate scale:—

Silicate Scale

Silicate of Lime	63.03
Sulphate of Lime	:	:	:	:	:	:	:	.32
Hydrated Oxide of Iron	36.53
								<u>99.88</u>

If the hydrated oxide of iron which exists in this scale as a distinct layer is eliminated and the analysis reconstructed, the percentage composition of the scale would be:—

Silicate of Lime	99.30
Sulphate of Lime	:	:	:	:	:	:	:	.50
								<u>99.80</u>

which is practically pure silicate of lime.

Silicate Scale

Alumina	10.18
Oxide of Iron	1.10
Silicate of Lime	60.00
Carbonate of Lime	17.10
Magnesia	11.17
	<hr/>
	99.55
	<hr/>

This is an instance of a very bad silicate scale which was very destructive to the tubes. The silica did not exist in the water, but was blown into the storage tanks in the form of a very fine sand. This sand dissolved up in the treated water, which contained a slight excess of caustic soda. An examination of the sediment at the bottom of the storage tanks revealed the presence of a considerable quantity of sand which had not dissolved up.

Similar deposits and scales are produced when fine clay is allowed to get into the boilers. Some bore wells deliver a water which is not quite clear, and which will not become clear by mechanical filtration. These waters are generally waters containing carbonate of soda, and when the cloudy water is fed into the boilers, the silica is first dissolved by the soda, and then precipitated as a silicate deposit by any lime or magnesia there may also be in the boiler. The following is an example from a bore hole in the Greensands. The water was a comparatively soft carbonate of soda water, but the fine sand contained a considerable percentage of ferrous silicate. When the sand was boiled with the alkaline soda-water under pressure in the boilers, it was decomposed, the silica was dissolved and the ferrous oxide set free; the result being that a bad silicate scale, having the following decomposition, was formed:—

Silicate Scale

Silicate of Lime	38.75
Silicate of Magnesia	18.20
Alumina	4.02
Carbonate of Lime	35.81
Sulphate of Lime	2.70
	<hr/>
	99.48
	<hr/>

The ferrous oxide which was set free is a powerful reducing agent, and a further effect was that some of the sulphates were reduced. Ferric Oxide and some ferrous sulphide were formed, and the quantity was sufficient to cause some tubes to become

blocked and cause an explosion. The dark green deposit thus formed had the following composition:—

Silica	1.80
Sulphide of Iron	5.34
Ferrous Oxide	38.83
Ferric Oxide	40.94
Carbonate of Lime	11.30
Magnesia52
Moisture48
	<hr/>
	99.21
	<hr/>

This deposit when first taken out was hard and completely choked the tubes. At first it did not contain any free sulphur, but on exposure to the air for some time it crumbled into a fine powder, and free sulphur could be dissolved out of it with bisulphide of carbon. Sulphur is extracted from coal gas by passing the gas through moist ferric oxide and exposing the ferrous sulphide so formed to the action of the air.

These fine clays are also brought down by tropical rivers, and as mechanical filtration is not effective, they often get into the boilers and cause a silicate scale. The following are examples from West Africa and South America:—

West Africa

Alumina and Oxide of Iron	11.17
Silicate of Alumina	10.27
Silicate of Lime	57.50
Silicate of Magnesia	3.13
Carbonate of Lime	14.10
Sulphate of Lime	1.77
Organic Matter	2.06
	<hr/>
	100.00
	<hr/>

South America

Alumina and Oxide of Iron	8.96
Silicate of Lime	34.41
Sulphate of Lime	29.78
Carbonate of Lime	21.02
Magnesia92
Organic Matter	4.91
	<hr/>
	100.00
	<hr/>

This scale is extremely hard. It is almost impossible to remove it from the tubes by scrapers, and even when removed it is exceedingly difficult to pulverize it.

Sulphate of Soda sometimes enters into the composition of boiler scales. It comes down in conjunction with sulphate of lime in the form of Glauberite, a mineral sometimes found in Nature. Glauberite is a double sulphate of lime and soda having the constitution $\text{CaSO}_4 \cdot \text{Na}_2\text{SO}_4$. The following is an example of an artificial Glauberite scale taken out of a boiler :—

Soda Scale

Silica69
Sulphate of Lime	43.81
Sulphate of Sodium	52.09
Magnesia	1.32
Water, etc..	2.09
	<hr/>
	100.00
	<hr/>

Although this scale was insoluble in the boiler water from which it was deposited, when put into distilled water it crumbled up and fell into powder, the sulphate of soda dissolving and the sulphate of lime being left. Such scales as this are only deposited from concentrated boiler waters containing large quantities of sulphate of soda.

Scales are also often found containing very large percentages of the oxides of iron, but as the oxides of iron are derived from the corrosion of the boiler, they are not true scales. The following are examples of this kind of scale formed in a boiler evaporating a slightly acid water containing sulphate of lime :—

Oxide of Iron Scales

Silica	1.95
Oxide of Iron	65.00
Basic Ferric Sulphate	3.00
Sulphate of Lime	25.94
Magnesium Hydrate	1.44
Water of Hydration, etc.	2.67
	<hr/>
	100.00
	<hr/>
Silica	15.12
Ferrous Oxide	14.97
Ferric Oxide	32.29
Basic Ferric Sulphate	5.37
Sulphate of Lime	23.12
Magnesium Hydrate	8.85
	<hr/>
	99.72
	<hr/>

These are really sulphate of lime scales containing oxide of iron. As these scales are hard the sulphate of lime must have acted as

a cement upon the oxide of iron, as oxide of iron is usually found in boilers as a loose powder or sludge. The following, however, is an oxide of iron scale containing no sulphate of lime nor anything else to cement it. The small percentage of oil may have been the cause of it being baked *in situ*.

Oxide of Iron Scale

Silica	25
Ferrous Oxide	26.78
Ferric Oxide	64.22
Magnesia	21
Oil	1.50
Water of Hydration	7.04
	<hr/>
	100.00
	<hr/>

This scale contains 98 per cent. of the hydrated oxides of iron, and was deposited from the following boiler water:—

Boiler Water

Nitrate of Lime	57.40
Sulphate of Lime	25.84
Chloride of Magnesia	62.90
Sulphate of Sodium	1757.25
Chloride of Sodium	3403.00
	<hr/>
	5306.39
	<hr/>

This boiler water is in a very corrosive condition, and no doubt other portions of the scale would have been found to contain some sulphate of lime.

The following scale is somewhat of a curiosity, as it contains over 60 per cent. of zinc hydrate and zinc carbonate.

Zinc Scale

Silicate of Lime	5.68
Sulphate of Lime	4.50
Carbonate of Lime	21.25
Magnesia	1.44
Zinc Hydrate	46.47
Carbonate of Zinc	17.87
Water of Hydration, etc.	2.79
	<hr/>
	100.00
	<hr/>

This scale was the result of putting slabs of zinc into a boiler evaporating water containing caustic soda. The analysis of the boiler water showed it to contain:—

Boiler Water

Caustic Soda	58.80
Carbonate of Sodium	5.56
Nitrate of Sodium	47.60
Sulphate of Sodium	76.34
Chloride of Sodium	52.42
	<hr/>
	240.72
	<hr/>

The bulk of the magnesia and a considerable portion of the carbonate of lime precipitated on boiling the water, do not form scale, but remain in the boiler water in a state of suspension. When at the same time oil finds its way into the boilers this sludge collects the oil and forms oily deposits. The oily deposits by lodging on the tubes or plates frequently cause overheating, and at the same time becoming burnt on to the iron prevent proper contact between the water and the boiler surfaces. In such deposits it is usual to find a considerable percentage of organic matter derived from the partial carbonization of the oil. When in addition to the mineral hydrocarbon the oil also contains saponifiable oil, insoluble lime and magnesia soaps are formed. These soaps are very sticky and easily adhere to the heating surfaces, where they form a nucleus for crystallizing scale, and in this way often form thick greasy nodules almost impermeable to heat. These nodules prevent the transmission of the heat to the water, the tube or plate becomes overheated and collapses either by being actually burnt or by becoming so weakened as to be unable to stand the pressure and strain. It is for this reason that oil is so injurious to steam boilers. If the boiler contained no insoluble matters it is extremely doubtful whether a small quantity of oil would have any deleterious effect at all.

The following are analyses of oily deposits actually taken out of boilers :—

Oily Deposits

Silica	5.45
Alumina and Oxide of Iron	18.68
Carbonate of Lime	15.24
Sulphate of Lime95
Magnesium Hydrate	4.37
Organic Matter.	7.20
Oil	44.20
Moisture, etc.	3.91
	<hr/>
	100.00
	<hr/>

Carbonate of Lime	42.00
Aluminate of Lime	10.80
Oleate of Lime	12.54
Oleate of Magnesia	10.83
Silicate of Magnesia	14.78
Oil	2.64
Moisture	6.41

100.00

Silica	11.12
Alumina and Oxide of Iron	6.88
Carbonate of Lime	8.00
Magnesium Hydrate	22.41
Oil	36.06
Organic Matter, etc.	15.53

100.00

Silica	2.88
Alumina and Oxide of Iron	8.12
Carbonate of Lime	17.86
Magnesium Hydrate	59.99
Oil	2.20
Organic Matter	8.95

100.00

Silica	11.00
Alumina and Oxide of Iron	26.16
Carbonate of Lime	2.00
Magnesium Hydrate	35.62
Organic Matter.	16.12
Oil	9.10

100.00

This last deposit was taken out of a turbine into which it had been carried by the steam from the boilers:—

Silica	12.70
Oxide of Iron	6.08
Metallic Iron	3.58
Metallic Copper	3.07
Carbonate of Lime	32.71
Magnesium Hydrate	17.21
Oil	12.40
Organic Matter.	6.54
Moisture, etc.	5.71

100.00

This is also a turbine deposit, the copper and iron being derived from some part of the turbine itself.

CHAPTER V

SOFTENING

A RAPID and convenient method of determining the total lime and magnesia salts in a water is by means of a solution of soap in dilute alcohol. A soap is a salt containing a base combined in equivalent proportions with a fatty acid or acids. Ordinary soap is a soda salt of oleic or stearic acids, and for the sake of simplicity may be regarded as oleate of soda. Oleate of soda is soluble in dilute alcohol, and when a small quantity of this solution is shaken up with distilled water a lather is formed. Oleate of lime and oleate of magnesia, on the other hand, are insoluble soaps which do not lather. When a solution of oleate of soda is added to a water containing a lime or magnesia salt, insoluble oleate of lime or magnesia is precipitated and no lather is formed, so long as any lime or magnesia remains to be precipitated. When the whole of the lime and magnesia have been precipitated in this way, any excess of the soap solution is free to form a lather with the water when shaken up with it.

A water which requires only a small quantity of soap solution to give a lather is described as a soft water, and when much soap is required the water is called a hard water. In this way has grown up the habit of regarding water as hard or soft, according to its soap-destroying power.

By standardizing the soap solution on a solution containing a known quantity of a lime salt, the soap solution can be used as a measure of the lime and magnesia in any water, and is said to record the hardness of the water; that is, the total lime and magnesia salts converted into their equivalent of carbonate of lime.

The soap solution does not discriminate between the lime or magnesia but records them both, and is at best only approximate. But by taking suitable precautions and exercising considerable care, especially with waters containing magnesia, it can be made to give a fairly close approximation to the total lime and

magnesia, recorded as carbonate of lime ; this result is known as the total hardness. By boiling the water for half an hour to precipitate the carbonates, filtering these off and making up the remaining water to its original volume with distilled water, the hardness after boiling can be estimated by soap. The difference between the total hardness and the hardness after boiling (*i. e.* the permanent hardness) is called the temporary hardness. Roughly speaking, the temporary hardness corresponds to the carbonate hardness, and the permanent to the sulphate hardness or its equivalent.

The process of removing the soap-destroying power or hardness of a water is called softening the water, and the process can be carried out more economically and expeditiously than by using soap, which is at best an exceedingly costly and troublesome method.

The best and cheapest method of softening water, except perhaps comparatively soft waters, is treatment by lime, either alone or in conjunction with carbonate of soda, if the nature of the water requires it. By this means it is possible to remove or destroy the lime and magnesia salts which cause the troublesome scales and deposits already described.

As previously explained, carbonate of lime is held in solution by virtue of free carbonic acid, so that if the water can be deprived of this free carbonic acid, the carbonate of lime (and magnesia) becomes insoluble in water and is therefore precipitated, rapidly crystallizes and can be removed by filtration, leaving the water quite clear and free from carbonate of lime.

This carbonic acid can be removed by boiling, but this is expensive and seldom practicable.

The following test was made on a London water which contained 8.62 grains of free carbonic acid per gallon :—

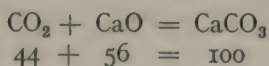
Heated to 212° F. .	.	.	5.85	Free Carbonic Acid
Boiled for 1 minute	.	.	5.39	" " "
" " 2 "	.	.	4.47	" " "
" " 3 "	.	.	3.54	" " "
" " 4 "	.	.	2.62	" " "
" " 5 "	.	.	1.23	" " "
" " 10 "	.	.	nil	" " "

so that continued boiling for 10 minutes is necessary to remove all the free carbonic acid ; that is, to attain the same result as can be instantly obtained by the addition of the requisite quantity of lime.

The lime unites with the carbonic acid to form carbonate of

lime, and the new carbonate of lime, together with the old carbonate of lime which has no carbonic acid to hold it in solution, falls as an insoluble precipitate. Therefore to remove carbonate of lime from any water, it is only necessary to know the quantity of free carbonic acid in the water and from this to calculate the lime required. When this quantity is added and agitated with the water the action is complete, and the water can either be allowed to settle or, better still, passed into filters, where the constant onward movement causes a fairly rapid crystallization of the carbonate and the water filters quite clear.

When the quantity of free carbonic acid is known, it is easy to calculate the amount of lime required. Thus:—



as 44 parts of carbonic acid require 56 parts of lime, each grain of carbonic acid requires 1.273 grains, and each 1000 gallons of water will require 1273 grains of lime for every grain of free carbonic acid. Now 1273 grains = $\frac{1273}{7000} = .182$ lb. Therefore if the number of grains of free carbonic acid is multiplied by the Factor .182 the result is the number of lbs. of real lime required per 1000 gallons of the water in question.

This calculation is based on a lime of 100 per cent., a theoretical curiosity never seen in practice. Lime is so variable in strength and composition, that it is impossible to add exact quantities. It is therefore advisable to use it in the form of calcium hydrate, a standard material containing exactly 70 per cent. of available lime. If the Factor for real lime is divided by .7 the result is the actual quantity of calcium hydrate required. Thus $.182 \div .7 = .26$, which is the Factor by which each grain of free carbonic acid must be multiplied to obtain the amount of calcium hydrate required to remove the carbonate hardness of a water.

For example, a water containing 8.5 grains of free carbonic acid per gallon, would require $8.5 \times .26 = 2.21$ lb. of calcium hydrate per 1000 gallons.

Lime can also be used in the form of lime-water, but this, in addition to other disadvantages, has the further disadvantage that the solution obtained is very dilute and varies in strength according to the temperature. The following table gives the amount of calcium hydrate in water at different temperatures.

These figures are given in terms of calcium hydrate, as lime is converted by water into the hydrate before it can dissolve. If the figures are required in terms of actual lime (CaO) they should be multiplied by .7.

Solubility of Calcium Hydrate

<i>Tempera- ture.</i>	<i>Grains per Gallon.</i>
32° F.	132.09
40° F.	127.95
50° F.	121.73
60° F.	115.51
70° F.	110.85
80° F.	107.74
90° F.	103.60
100° F.	99.97
110° F.	96.87
120° F.	93.72
130° F.	86.51
140° F.	82.88
150° F.	78.74
160° F.	70.87
170° F.	68.79
180° F.	63.71
190° F.	59.57
200° F.	56.98
212° F.	52.32

The figures in this table are calculated from the mean of two closely agreeing determinations by Standard Acid, using phenolphthalein as indicator. The water was recently boiled before digestion with the calcium hydrate, which was used in considerable excess, and allowed to remain in contact with the water for one hour, being vigorously shaken from time to time in a bottle with a closely fitting stopper and filled to the top in order to preclude any disturbance by the action of air.

So that lime-water at 212° F. only contains a little more than one-third as much as water at 32° F., and a rise of temperature from 50° to 70° decreases the solubility nearly 10 per cent. This would mean that the amount of saturated lime-water used in the softening process is 10 per cent. greater at 70° than at 50°, and considerable adjustment of valves would therefore be necessary to obtain the best results in the softening process.

The slight solubility has also the disadvantage that a very large proportion of the water to be treated has to be converted into lime-water.

The following table gives the quantities of lime-water required for the free carbonic acid :—

Lime-water Table

Free CO ₂ in Grains per Gallon.	Gallons of Saturated Lime-water required per 1000 gallons of Hard Water at 55° F.
1	14.20
2	28.40
3	42.60
4	56.80
5	71.00
6	85.20
7	99.40
8	113.60
9	127.80
10	142.00
11	156.20
12	170.40
13	184.60
14	198.80
15	213.00
16	227.20
17	241.40
18	255.60
19	269.80
20	284.00

Note.—55° F. has been selected for the temperature in these calculations, as 55° is nearer the average temperature of water flowing through mains than 60° F.

At 60° F. the figure for each grain of free carbonic acid is 14.56 gallons, upon which basis another table can easily be constructed. As 1273 grains of real lime are equivalent to 1682 grains of calcium hydrate, a table can be constructed for any temperature given in the solubility table, by dividing 1682 by the solubility of calcium hydrate for that temperature.

TESTING LIME-WATER

A convenient method of testing the lime-water is to take 25 c.c., add phenolphthalein, and then run in N/10 acid from the burette until the red colour formed with the phenolphthalein is just discharged. The discharge of colour marks the exact point at which the dissolved lime is neutralized. The following table gives the results which should be obtained if the lime-water is saturated at the temperatures given.

Tempera- ture.	N/10 Acid Required.
32° F.	12.75 C.C.
40° F.	12.35 "
50° F.	11.75 "
60° F.	11.15 "
70° F.	10.70 "
80° F.	10.40 "
90° F.	10.00 "
100° F.	9.65 "

If this method is strictly adhered to, the number of c.c. of N/10 acid used multiplied by 7.84 will give the amount of real lime in grains per gallon. Thus at 60° F. 11.15 c.c. are required; this figure multiplied by 7.84 gives 87.4 grains per gallon.

To arrive at the amount of calcium hydrate in solution, the Factor is 10.36. Thus $11.15 \times 10.36 = 115.5$ grains of Calcium Hydrate per gallon.

In works where N/10 acid is not available and only N/50 acid is used, the test can be carried out with this acid, but as five times as much acid is required for each test, the process is cumbersome and expensive. It is therefore better to take 10 c.c. of the lime-water. The results will then be as follows:—

Temperature.		N/50 Acid Required.
32° F.	25.5 c.c.
40° F.	24.7 "
50° F.	23.5 "
60° F.	22.3 "
70° F.	21.4 "
80° F.	20.8 "
90° F.	20.0 "
100° F.	19.3 "

The number of c.c. N/50 acid used multiplied by 3.92 will give the amount of real lime in grains per gallon, and multiplied by 5.18 the amount of Calcium Hydrate, also in grains per gallon. If on testing samples of lime-water in this way, a less quantity of acid is required, then the lime-water is not saturated, and if a greater quantity of acid is required, there must be some soda getting in with the lime or calcium hydrate.

The following example is from actual practice:—

Lime-water (25 c.c. used)

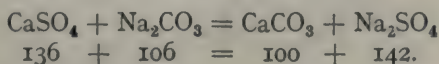
No. 1	32.5 N/10 Acid.
" 2	31.25 " "
" 3	32.50 " "
" 4	31.25 " "
" 5	32.50 " "
" 6	31.25 " "

These samples were taken every hour for six consecutive hours. As these figures are in excess of the figures for saturated lime-water, a further examination was made and revealed the presence of caustic soda. Investigation showed that by mistake on that particular day, some soda had been put into the lime-water tank.

This method of testing the lime-water should never be neglected, when using a lime-water plant, as the strength may vary so much that considerable regulation of the valves may be necessary owing to variations in the temperature. As some waters containing a good deal of free carbonic acid require as much as 15 per cent. of their volume to be made into clear lime-water, this precaution is not to be disregarded if the water is to be kept in reasonably good condition.

As the total hardness of comparatively few waters is temporary—that is, carbonate hardness—the remaining or permanent hardness has also to be dealt with. This hardness is generally due to sulphate of lime, and sulphate of magnesia, but may also be due to nitrate of lime, nitrate of magnesia, chloride of magnesia, and in exceptional circumstances, to chloride of calcium.

Dealing first with sulphate of lime. As this salt is soluble in water alone, calcium hydrate will have no effect upon it and carbonate of soda will have to be employed.



Each 136 parts of sulphate of lime requires 106 parts of carbonate of soda. The carbonate of soda is generally used in the form of soda ash, and as the 58 per cent. alkali of commerce is guaranteed to contain 98 per cent. of carbonate of soda and generally does so, it may be considered a sufficiently reliable basis on which to make the calculations. Therefore each grain of sulphate of lime requires $\frac{106}{136} = .779$ grains of soda ash. That is, 1000 gallons will require $\frac{.779}{7000} \times 1000 = .111$ lb. soda ash.

The amount of sulphate of lime multiplied by the Factor .111 will give the lb. of soda ash required per 1000 gallons of the water.

Calculating the quantities for the other salts which may form the permanent hardness, the following factors are obtained:—

Nitrate of Lime	F = .092
Chloride of Calcium	F = .136
Sulphate of Magnesia	F = .126
Nitrate of Magnesia	F = .102
Chloride of Magnesia	F = .159

By means of the soda ash these salts are decomposed, *after* the free carbonic acid has been eliminated by the calcium hydrate. If the carbonic acid has not been removed a portion of the soda

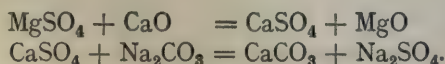
ash is converted into bicarbonate of soda, and as this does not completely precipitate any of the above materials, so much of the soda is wasted and the water is not properly softened.

The following table gives the amount of soda ash which would be converted into bicarbonate by free carbonic acid in each 1000 gallons of water, that is to say, how much would be rendered useless.

Amount of Soda Ash put out of Action by the Free Carbonic Acid in 1000 Gallons of Water

Free Carbonic Acid. Grains per Gallon.	Soda Ash. lb.
1	.34
2	.69
3	1.03
4	1.38
5	1.72
6	2.06
7	2.41
8	2.75
9	3.10
10	3.44
11	3.78
12	4.13
13	4.47
14	4.82
15	5.16
16	5.50
17	5.85
18	6.19
19	6.54
20	6.88

Carbonate of magnesia is soluble in pure water to the extent of 6.0 grains per gallon, so in order to obtain the best results it is necessary to first precipitate the magnesia as hydrate by means of calcium hydrate. Magnesia as hydrate is much less soluble in water than the carbonate, and much better softening results are obtained if sufficient calcium hydrate is used to eliminate the magnesia. The magnesia thus precipitated, the soda ash eliminates the lime (calcium hydrate) which has been used to turn out the magnesia.



Thus each 120 parts of sulphate of magnesia require 56 parts of lime, that is $\frac{56}{7} = 80$ parts calcium hydrate, so that each grain

of sulphate of magnesia requires .666 grains calcium hydrate or .095 lb. per 1000 gallons. The other Factors are :—

Nitrate of Magnesia	F = .077
Chloride of Magnesia	F = .120

The complete list of Factors will be as follows :—

For Calcium Hydrate

Free Carbonic Acid	F = .260
Magnesium Sulphate	F = .095
Magnesium Nitrate	F = .077
Magnesium Chloride	F = .120

For Soda Ash

Calcium Sulphate	F = .111
Calcium Nitrate	F = .092
Calcium Chloride	F = .136
Magnesium Sulphate	F = .126
Magnesium Nitrate	F = .102
Magnesium Chloride	F = .159

With these Factors it becomes a simple matter to calculate the amount of softening materials required by any given water. The following analysis of a well water will illustrate the method of calculation.

Analysis

Sulphate of Lime	27.05
Carbonate of Lime	9.10
Sulphate of Magnesia	6.81
Nitrate of Magnesia	6.43
Chloride of Magnesia	4.03
Free Carbonic Acid	6.31
Total Hardness	40.63°

Calcium Hydrate

Carbonic Acid	$6.31 \times .26 = 1.64$ lb.
Sulphate of Magnesia	$6.81 \times .095 = .65$ "
Nitrate of Magnesia	$6.43 \times .077 = .50$ "
Chloride of Magnesia	$4.03 \times .120 = .48$ "

Total Calcium Hydrate 3.27 "

Soda Ash

Sulphate of Lime	$27.05 \times .111 = 3.00$ lb.
Sulphate of Magnesia	$6.81 \times .126 = .85$ "
Nitrate of Magnesia	$6.43 \times .102 = .65$ "
Chloride of Magnesia	$4.03 \times .159 = .64$ "

5.14 "

and the quantities required per 1000 gallons of the water are:—

Calcium Hydrate	3.27 lb.
Soda Ash	5.14 „

These figures are the exact quantities equivalent to the materials contained in the water, but as they exactly balance, the process is not quite complete; that is to say, if these quantities are only balanced, the whole of the hardness is not removed and it requires a slight excess of chemicals to weigh down the balance and ensure the best results. The excess may be cut very fine, but to obtain the lowest possible residual hardness, and to leave a slight soda alkalinity in the treated water, it is advisable to make this excess 10 per cent. In the case of the water represented by the above analysis, this water was actually treated with the 10 per cent. excess, the result being that the hardness was reduced from 40.6° to 1.0°, with a soda alkalinity of 2.0°.

If an excess of chemicals is not added, the residual hardness left in the water may cause corrosion. For example, take the following water:—

Carbonate of Lime	13.86
Nitrate of Lime	4.98
Sulphate of Magnesia	1.68
Chloride of Sodium	4.09

If the chemicals, especially the Soda, are cut too fine, the residual hardness will be almost entirely due to nitrate of lime, which in this case will cause considerable corrosion in the boilers and in time perforate the tubes. There is here the danger of removing the carbonates, which would act as a protection to the iron and leaving nitrate of lime to act on the unprotected metal. If this water is to be treated at all it should be properly softened, that is, practically the whole of the hardness should be removed, or it had better be left alone. To lay down a rule that no water should be softened below, say, 5° is a heresy that has led and will lead to very serious trouble to boilers. Before making such a recommendation the analysis of the water should be very carefully considered, and if when the carbonate hardness, which is the easiest to destroy, has been removed, it would leave either nitrate of lime or nitrate of magnesia or chloride of magnesia, either actual or potential, or any combination of these, it is better to leave the water alone than reduce it to, say, 5° or 6°. The proper plan is to use a slight excess of chemicals, so as to destroy the corrosive materials and give the water a slight soda alkalinity.

Referring again to this water, if the carbonate hardness alone is removed, which is the most likely thing to happen if the water is not properly softened, the residual water would contain :—

Nitrate of Lime	4.98
Sulphate of Magnesia	1.68
Chloride of Sodium	4.09

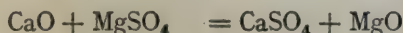
If this water is used in a boiler for 1000 hours, the boiler water at the end of that time would have a concentration of about 500 and would contain approximately :—

	Grains per Gallon.
Nitrate of Lime	2490
Sulphate of Magnesia	840
Chloride of Sodium	2045
	<hr/>
	6375
	<hr/>

which would be a very corrosive water indeed, as it would not only contain a large quantity of nitrate of lime, but would contain 665 grains of potential chloride of magnesia, formed by the reaction between the sodium chloride and sulphate of magnesia, whereby chloride of magnesia and sulphate of soda are formed, The boiler water would therefore contain two very corrosive salts, chloride of magnesia and nitrate of lime, which would so soon pit and puncture the metal that the lifetime of the boiler would be very short. Many boilers have been ruined in this way, by a rigid adherence to the rule that the water was not to be softened below 4° or 5° . In the case under consideration, if the water had been properly treated and practically the whole of the hardness removed and a slight soda alkalinity given to it, the boiler water would still have the same concentration, but the salts would be nitrate, sulphate and chloride of sodium, which would not attack the boilers and no corrosion would ensue.

When the proper mixture of calcium hydrate and soda ash has been determined, these are mixed together and stirred up in a suitable quantity of water. A suitable proportion is 1 lb. of this mixture per gallon of water, and as a gallon of water weighs 10 lb., this is roughly a 10 per cent. mixture. Even with mixtures containing a larger percentage of soda, this quantity of water is found to be quite sufficient even in the coldest weather. The solubility of soda ash in water at 32° is 7 per cent., and as the mixture seldom contains 50 per cent. of soda ash, this could at best only produce a solution of soda ash of $3\frac{1}{2}$ per cent. strength.

But the calcium hydrate when mixed with the soda ash and water immediately causticizes a portion of the soda ash, so that the final solution contains much of the soda ash in the form of caustic soda, which is even more soluble than the soda ash. When the ratio of the calcium hydrate to soda ash is greater than 74 : 106, the whole of the soda ash is converted into caustic soda, and the mixture which goes forward into the reaction tank of the Softener is a solution of caustic soda and calcium hydrate, with more or less calcium hydrate in the form of milk of lime (together with the insoluble carbonate of lime formed by the reaction). The first action that goes on when this mixture comes into contact with its calculated volume of water to be softened, is the reconversion of the caustic soda into carbonate by the free carbonic acid in the water; this is immediately reconverted into caustic soda by the excess of calcium hydrate, and the reaction goes on until the whole of the free carbonic acid has been converted into carbonate of lime. But a portion of this calcium hydrate has already been converted into carbonate by the original soda ash, so that there is *now* not sufficient to take away the whole of the carbonic acid from the reformed soda ash, and if the proportions have been properly calculated, there is exactly as much reformed soda ash left as was originally put into the mixture. This being the case and the calcium hydrate having done its work in eliminating the free carbonic acid, the soda ash is left to do its work in destroying these salts constituting the permanent hardness. In the cases where extra calcium hydrate is also put in to throw out the magnesia, the action is similar, and the soda ash calculated for the purpose throws out the lime from the lime salt formed by the action of the calcium hydrate in precipitating out the magnesia, thus:—



and



Thus, although soda ash does not completely precipitate magnesia salts, it can be made to do so by using with it an equivalent of calcium hydrate. The calcium hydrate does the work of turning out the magnesia, and the lime in its turn is thrown out by the carbonate of soda.

This reaction may also be explained as the action of caustic soda in precipitating the magnesia, but whichever explanation

be adopted, the fact remains that by using lime in conjunction with soda ash, the magnesia is almost wholly eliminated.

The precipitation of the carbonate of lime where lime-water is used is not immediate, and it takes several minutes for a cloudiness to appear. This cloudiness is the first indication that the reaction is taking place, and this action is accelerated both by heat and agitation. The precipitate first appears as an impalpable cloudiness in suspension in the water, and in this state it does not filter clear, but by agitation or by heat or by both, the precipitate assumes a crystalline form, and once the crystalline stage is reached the precipitate settles rapidly and the water can be filtered quite clear. The crystallization or aggregation into denser particles is also facilitated by adding some previously precipitated carbonate of lime, and this is the reason why old filters of wood wool upon which the carbonate has already crystallized give a clearer and softer effluent than new filters. It is also found in practice that milk of lime gives quicker and better results than lime-water; this is probably due to the fact that the milk of lime will always contain some carbonate of lime either from the lime itself or formed by the action of the lime upon the carbonic acid in the water used for making the milk of lime. Where clear lime-water is used, this carbonate of lime is allowed to settle out and does not come into action in the settlement of the main precipitate. Also when milk of lime is used in conjunction with soda ash, a quantity of carbonate of lime equivalent to the soda ash used is formed, and this is very useful in accelerating the precipitation and subsequent clarification of the treated water. For these reasons continuous plants using milk of lime, or milk of lime in conjunction with soda ash (for soda ash is nearly always necessary unless the water contains carbonate of soda), give better and more rapid results than plants where the lime is used as lime-water and is used separately from the requisite soda ash, and where the water is allowed to stand in settling tanks. In the former case one hour is usually sufficient to ensure a clear well-softened water, but in the latter case the water will not clarify in even three hours. Movement of the water, especially over a surface coated with previously precipitated carbonate of lime, such as a wood wool filter which has been for some time in use, is an important factor in the process. A time, of course, will arrive at which the filter will be so charged with this precipitate that the bulk of it has no opportunity of coming into contact with the crystalline surface, and when this stage is reached the

water no longer passes through clear. The filter then requires to be cleaned; that is, the superfluous sludge has to be blown or washed out by one of the devices used for cleaning filters.

By proper treatment of the water in the softening process it is generally possible to remove nearly all the lime and magnesia from the waters. It must not, however, be assumed that the theoretical quantities calculated for the process will achieve this result, as it is necessary to have a slight excess of chemicals to press down the balance and so precipitate all but the last traces; that is to say, all but the amounts which would be dissolved in pure water alone, or at least in water containing small quantities of sodium salts. The softening process can be made to remove the whole of the carbonate of lime, but it only destroys the salts constituting the permanent hardness; that is to say, it exchanges the lime or magnesia for soda and leaves the soda in combination with the acids originally combined with the lime and magnesia. Thus nitrate of lime and chloride of magnesia become respectively nitrate of sodium and chloride of sodium. If a slight excess of the softening chemicals is not used to press down the balance, the balance will be on the other side and will leave a small amount of lime or magnesia in its original combination, which is not what is required, as these accumulate on concentration in the boiler water. A properly softened water should always contain a slight excess of soda and should always give a pink colour with phenolphthalein. Unless the treated water gives this colour it has not been properly softened.

Further, it should be observed that the lime used for softening a water, although it goes into solution originally, does not go forward with the clear treated water but remains as a sludge. If any lime goes forward it goes forward as lime-water and the water is thereby rehardened. This rehardening may be necessary for a water which has afterwards to be mixed with condensed water, but for softening only no excess of lime should go forward, and the residual alkalinity of the softened water should always be due to a slight excess of soda and not to an excess of lime. Calcium hydrate being such an active material and uniform in strength, renders this perfectly practicable and easy to carry out on the large scale. With crude lime, on the other hand, this would be very difficult.

Waters containing magnesia, especially in the form of carbonate, do not soften so well as waters containing lime only. The reason for this is no doubt the greater solubility of carbonate

of magnesia in water *per se*. Magnesium hydrate is much less soluble, and in order to obtain the best results in softening it is necessary to use an excess of lime sufficient to precipitate the magnesia as hydrate, and then to remove the excess of lime by carbonate of soda in the usual way.

In testing magnesia waters by the soap test, it is necessary to be quite sure that the lather is a permanent one. A premature lather is often obtained which does not persist for the full five minutes, and when again shaken up with more soap solution no lather is obtained until a much larger quantity of soap solution has been added. In some cases the apparent lather appears when only 3 measures of soap solution have been added, but the permanent lather requires nearly 10 measures. The last result is the correct one, and the result taken from the premature lather would be very misleading, as it would record the hardness as 3.0° instead of 10°.

With these waters the magnesia soap is apparently not formed immediately, and it requires some time for the reaction to take place, but when once started it proceeds rapidly and there is no mistake about the final result. The magnesia soap can generally be distinguished by its curdy appearance.

PERMUTIT

Another method of softening water is by means of "Permutit," which is an artificial double silicate of alumina and soda. A portion of the soda is combined in the complex molecule in such a way that the permutit has the property of exchanging this soda for other metals, as, for example, lime and magnesia. When a hard water is slowly percolated through a layer of this material the lime and magnesia are retained by the permutit and the soda comes into the water in their place, the result being that the water emerges from the filter quite soft.

Certain natural zeolites and sands also possess this property, though in a modified degree, and hardly sufficient to render them available for water softening in competition with the artificial permutit.

The permutit only possesses the property of exchanging bases, the acids originally combined with the lime and magnesia remain in the percolated water in the form of soda salts. As for example, any bicarbonate of lime in the original water comes out in the percolated water as bicarbonate of soda, and chloride of magnesia

as chloride of sodium. The action of the permutit has been to entirely remove the lime and magnesia and leave soda in their place, and the effluent water contains no hardness at all.

After a time, when the soda in the permutit has been replaced by lime, it of course loses this property of softening the water. The process is then reversed and a solution of sodium chloride is slowly percolated through the filter. The reverse action takes place, the lime is exchanged for soda, the soda goes into the permutit, and the lime comes into the percolating solution of salt in the form of chloride of calcium. This is continued until the lime is removed and the soda restored to its original place in the molecule. After the solution of salt has been washed out the filter is again ready for use as a water softener.

How long these reactions can be carried on without damaging the activity of the exchangeable silicate, experience has not yet shown. At present the permutit is regenerated when it begins to pass water showing any hardness at all to the soap test, but possibly the layers of permutit could be worked until the water showed, say, 5° or 6° Hardness, by a system of by-passing in which the layers were in series. When a layer ceases to pass water of zero hardness, it could be moved further back in the series and its place taken by a layer of new or regenerated material, just in the same way as the layers of oxide of iron are used in the purification of coal gas from sulphuretted hydrogen. How far this can be carried out and what effect it would have on the lifetime of the complex silicate is a matter which can only be determined by experience. There may be mechanical difficulties in the way of using the permutit in this manner, but they are not insuperable.

An objection to the use of permutit is the high soda alkalinity obtained by treating hard carbonate of lime waters. This might be regulated by first removing the bulk of the carbonate by calcium hydrate and then passing the resultant water through the permutit. By this means the alkalinity could be regulated to any desired degree. And in special cases where it is necessary to have a water containing no hardness at all, the water might be first treated by the lime-soda process and finished off by permutit.

CHAPTER VI

SOLUBLE SALTS

THE soluble salts, that is, the salts soluble in water *per se* and not precipitated on boiling, are the chloride and nitrate of lime, chloride, sulphate and nitrate of magnesium, and sulphate nitrate and chloride of sodium. Any or all of these may occur in a natural boiler feed water, and as the water is evaporated in the boilers, they become concentrated and can become very strong solutions of these salts and may and often do exercise a very corrosive action upon the boiler tubes and plates. It is well known that in many cases where explosions have taken place the tubes or plates have been so reduced in thickness that they have been unable to withstand the pressure and so given way with disastrous results. This thinning of the metal is the result of chemical action. Pure water would not dissolve up the iron so as to reduce the thickness from $\frac{7}{16}$ to $\frac{1}{8}$ inch or even less. Nor would stress or strain accomplish this, although these strains might cause the plates to crack; the mere strain would not dissolve the iron, as must undoubtedly be the case where a $\frac{7}{16}$ inch or $\frac{1}{2}$ inch plate is reduced to the thickness of paper. Incrustation on the plates would also tend to cause them to crack or cause failure of the tubes by inducing external corrosion, but none of these causes will explain the eating away of the metal from the inside to such an extent that it is no longer of any service.

The cause of the chemical action must be looked for in the water which is used for feeding the boiler. It has already been shown that all natural waters must and do contain a number of materials, some of which are more soluble in cold than in hot water, and others which are more soluble in hot than cold water. Those that are more soluble in cold water naturally become less soluble when the water is heated and concentrated in the boilers. These salts do not pass away with the steam, but accumulate in the boiler water, and in this way incrustations of what are

generally considered to be soluble salts are sometimes formed in boilers. Any salt, however soluble, must in course of time come out of solution when the point of saturation is reached, but the incrustations referred to are formed long before the point of saturation, or what would be considered to be the point of saturation for that particular salt in pure water, is reached.

The following are cases from actual practice :—

Feed Water

Silica	24
Oxide of Iron	18
Sulphate of Lime	24.58
Carbonate of Lime	5.04
Sulphate of Magnesia	21.18
Sulphate of Sodium	74.19
Chloride of Sodium	45.86
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	171.27
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On evaporation the sulphate and carbonate of lime come down as an insoluble scale or sludge and the other constituents become more and more concentrated as the water evaporates, and at the end of about 400 hours steaming this particular boiler water was found to be unworkable and very corrosive. A sample taken showed it to contain :—

Boiler Water

Ferrous Sulphate	21.28
Sulphate of Magnesia	2,013.00
Sulphate of Sodium	8,789.63
Chloride of Sodium	4,914.00
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	15,737.91
	<hr/>

The sample as actually received contained some crystalline matter, which was weighed, analyzed and found to consist of—

Sulphate of Magnesia	38.34
Sulphate of Sodium	2,444.93
	<hr/>
	2,483.27
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As this quantity was actually in solution when the sample was drawn from the boiler, it has been included in the analysis of the boiler water given above.

The scale deposited from this boiler water had the following composition :—

Hard Scale

Silica	1.35
Oxide of Iron56
Carbonate of Lime	15.30
Sulphate of Lime	14.45
Sulphate of Sodium	66.56
Magnesia	2.20
	<hr/>
	100.42
	<hr/>

The scale contains 50 per cent. of sulphate of soda, over and above that required to form the artificial Glauberite, and this sulphate of soda must have been deposited owing to its insolubility in the boiler water. If it had been left in the scale merely by some of the boiling water drying up with it, then there should have been a corresponding quantity of chloride of sodium, but there is none.

This boiler water was much too concentrated. It will be seen that it deposited a good deal of sulphate of sodium on standing, and as sulphate of sodium is more soluble in cold water than it is in hot, it is exceedingly probable that more of the sulphate of sodium was deposited as a crystalline scale while the boiler was under steam. When the boiler was shut down to cool, this sulphate of sodium would redissolve and not be found as a scale when the boiler was opened. At the same time, although the water from the boiler was not nearly saturated with sulphate of magnesia, nevertheless it crystallized out to the extent of 38 grains per gallon. As already mentioned, sulphate of sodium is soluble in cold water to the extent of 37,275 grains per gallon, and in water at 212° F. to the extent of 29,855 grains, but here it crystallizes out of a solution containing only 8789 grains per gallon. It is therefore probable that the solubility of sulphate of soda, and possibly other soluble salts such as the chloride and nitrate, is not so much a question of the solubility in water alone, as of the solubility of one of these salts in a solution of the others.

The following are the particulars of another case :—

Boiler Water

Silicate of Soda	8.82
Aluminate of Soda	139.05
Caustic Soda	486.70
Carbonate of Soda	333.90
Nitrate of Sodium	844.90
Nitrite of Sodium	47.60
Sulphate of Soda	10,151.48
Chloride of Soda	2,682.23
	<hr/>
	14,694.68
	<hr/>

<i>Scale</i>	
Silica	1·06
Alumina	4·10
Carbonate of Lime	1·18
Nitrate of Sodium	2·55
Sulphate of Sodium	63·24
Carbonate of Sodium	5·09
Chloride of Sodium	9·36
Water	13·42
	<hr/>
	100·00
	<hr/>

This is a saline scale containing 80 per cent. of soda salts soluble in water. It dissolved up again when the boiler was emptied and filled up with fresh water. Sulphate of soda has in this case come out of solution at a point far below the point of saturation for pure water, and as there is no sulphate of lime, the formation of Glauberite can have had nothing to do with it. The deposition of sulphate of soda from a boiler water is evidently not a deposition from water alone, but from a solution of other soluble salts. No boiler water consists of water alone, but is always a more or less complicated solution of many salts, and the point of saturation or what amounts to the same thing, the point of deposition of one of these salts, generally the sulphate of soda, is very much below the point of saturation for water alone.

An experiment was made on the following boiler water :—

<i>Boiler Water</i>	
Caustic Soda	163·52
Carbonate of Soda	108·33
Sulphate of Sodium	365·80
Nitrate of Sodium	47·60
Chloride of Sodium	429·97
	<hr/>
	1115·22
	<hr/>

This boiler water was further concentrated at ordinary atmospheric pressure until it began to deposit crystals. At this point the solution contained :—

<i>Concentrated Boiler Water</i>	
Caustic Soda	1102·0
Carbonate of Soda	730·0
Sulphate of Soda	2475·0
Nitrate of Soda	320·0
Chloride of Sodium	2898·0
	<hr/>
	7525·0
	<hr/>

and the deposited crystals consisted of sulphate of sodium.

Here again the sulphate of sodium comes out of solution at a point far below the point of saturation, and in this case at ordinary atmospheric pressure, and at a temperature of about 220° F. Always bearing in mind the fact that sulphate of sodium becomes less and less soluble as the temperature rises and that it becomes insoluble in water alone at 570° F., it is only reasonable to conclude that sulphate of sodium comes out of solution in high-pressure boiler waters, containing as they invariably do other salts, at a point of concentration very far short of its solubility in boiling water. This is further confirmed by the fact that sulphate of sodium is not infrequently found as a constituent of boiler scales.

So far only two soluble salts, viz. the sulphate and chloride of sodium, have been dealt with, but a boiler water often contains nitrates in addition, so that the solubilities will no doubt be further affected. Further complications may be brought about by the presence of carbonate of sodium or caustic soda, which are nearly always present in a boiler water. The question of concentration therefore becomes very complicated, and it is difficult to say where the limit should be drawn or to fix a point beyond which it is dangerous to go. This point will be largely determined by the pressure at which the boilers are worked, for the higher the pressure the higher the temperature, and when it is known that sulphate of soda becomes insoluble at 570° F. in water alone, the point of safety should be fixed very much below the solubilities in water at 212° F.

Practical working experience has shown that when the soluble solid constituents in a boiler water working at 200 lb. pressure are kept below 1000 grains per gallon there is no danger of the deposition of either chloride or sulphate of sodium, and it is advisable that this point should not be exceeded. If, however, there is very little sulphate of soda, and the soluble salt is chiefly chloride of sodium, this limit may be exceeded, but the dominant fact that the solubility of sulphate of soda diminishes as the temperature rises should never be lost sight of. A practical recognition of this fact in the working of boiler waters may save many boiler tubes from hogging and blistering. A deposition of sulphate of soda may also account for the cracking of plates, an explanation for which has hitherto been lacking. This is a matter on which further investigation should be made and would well repay any trouble taken in the matter, as it is a possible explanation of many things that may take place inside a boiler.

No doubt it is a difficult research to carry out, and steam users are somewhat reluctant to allow their boilers to be experimented with in a way which would indubitably cause damage. As the pressures at which boilers are worked are becoming greater and greater the subject becomes more and more important, and some limit will have to be placed upon the concentration to ensure proper efficiency. It is not always convenient to have an analysis made of the boiler water, but if the total solids in the feed water are known and the evaporation of the boiler and its capacity known, the concentration can be calculated by the following formula :—

Let x = Evaporation per hour in gallons.

px = Contents of boiler at working level.

t = Number of hours steaming.

n = Total solids in the feed water in grains per gallon.

n_1 = Total solids in the boiler water after t hours steaming.

c = concentration.

Then
$$c = \frac{x \times t}{px} = \frac{t}{p}.$$

and
$$n_1 = c \times n = \frac{t}{p} \times n.$$

As an example, take the case of a boiler evaporating 950 gallons per hour and containing 2350 gallons of water at the working level. Total soluble salts 20 grains per gallon and steaming hours at 1000.

Here $x = 950$ and $px = 2350$.

$$\therefore p = \frac{2350}{950} = \frac{47}{19}$$

and
$$c = \frac{1000 \times 19}{47} = 404.$$

That is, the concentration in 1000 hours would be 404,

and
$$n_1 = 404 \times 20 = 8080,$$

that is at the end of 1000 hours steaming the total solids would amount to 8080 grains per gallon. The actual amount of soluble solids in the boiler itself would be 8080×2350 grains, or

$$\frac{8080 \times 2350}{7000} = 2712 \text{ lb.}$$

The following is an example from a boiler under continuous steam for 1085 hours without blowing off.

In 165 hours the boiler water contained :—

Calcium Hydrate	5.92
Nitrate of Sodium	17.85
Sulphate of Sodium	23.72
Caustic Soda	15.44
Chloride of Sodium	32.76
	<u>95.69</u>

In 381 hours :—

Calcium Hydrate	4.21
Nitrate of Sodium	41.65
Sulphate of Sodium	47.60
Caustic Soda	39.68
Chloride of Sodium	53.23
	<u>186.37</u>

In 550 hours :—

Calcium Hydrate	5.88
Nitrate of Sodium	53.55
Sulphate of Sodium	77.37
Caustic Soda	35.12
Chloride of Sodium	70.43
	<u>242.35</u>

In 832 hours :—

Calcium Hydrate	4.88
Nitrate of Sodium	89.25
Sulphate of Sodium	120.45
Caustic Soda	43.10
Chloride of Sodium	114.66
	<u>372.34</u>

In 1085 hours :—

Calcium Hydrate	4.52
Nitrate of Sodium	98.17
Sulphate of Sodium	146.03
Caustic Soda	46.08
Chloride of Sodium	126.95
	<u>421.77</u>

Even at the end of this time, without any blowing off, the boiler water was still in good condition, and the boiler could have been run another 1000 hours without blowing off, had it been

necessary. At the end of 1085 hours the boiler was blown down 9 inches, as shown in the gauge glass, then filled up with fresh feed water, and after another 15 hours steaming the boiler water contained :—

Calcium Hydrate	3'33
Nitrate of Sodium	77'35
Sulphate of Sodium	112'77
Caustic Soda	32'24
Chloride of Sodium	94'18
	<hr/>
	319'87
	<hr/>

The calcium hydrate can never increase beyond 6 or 7 grains, which is the limit of its solubility in high-pressure boilers.

Blowing off once has removed 25 per cent. of the soluble salts in the boiler water, and this one blow off has done more good than blowing off a little each day. Until the boiler water gets fairly strong it is only a waste of hot water to blow off at all, except when the feed water is very bad and contains such large quantity of soluble salts that constant blowing off is a necessity. In the above case the feed water was a London Water which had been softened, and then mixed with condensed water. The amount of make-up of course would be variable, and as the load would also vary a little, the actual figures do not quite correspond, but they are sufficiently close to show that the concentration given by the formula is sufficiently exact to give a fairly correct idea of the state of the boiler water.

According to the formula, the total solids should have been :—

<i>Hours.</i>	<i>Calculated.</i>	<i>Found.</i>
165	60	96
381	139	186
550	200	242
832	303	372
1085	395	422

supposing that the feed water had been constant and that the evaporation had been regular. The feed water was supposed to contain 1·4 grains soluble solids per gallon, the evaporation 950 gallons per hour, and contents of boiler at working level 3655 gallons. At the end of nearly 1100 hours the calculated and found figures more nearly approximate than during any other part of the run, and this would be likely to be the case as the feed water and the evaporation would have had a better chance of averaging themselves during the longer run. At the end of

the run the actual figures found only differ from the calculated by about $7\frac{1}{2}$ per cent.

It should not be overlooked that this formula is only correct when the feed water is constant and when the actual evaporation is known, but with a fairly regular feed water and a known evaporation it furnishes a ready means of arriving at the state of the boiler water, and a factor can be found which multiplied by the number of hours steaming will give the total solids in the boiler water.

In the above case the formula becomes :—

$$n_1 = \frac{t \times 950 \times 1.40}{3655}$$

$$= .364 t,$$

so that by multiplying the steaming hours in this case by .364, the total solids are at once approximately obtained.

Thus in 2000 hours, the total solids would be :—

$$2000 \times .364 = 728 \text{ grains per gallon.}$$

In drawing samples of boiler water from the gauge fittings, care must be taken that the top arm is kept closed, otherwise some steam comes over with the water and the sample is misleading.

Also care must be taken not to draw off the sample too quickly as part of the water will flash into steam if the pressure is suddenly released, and the boiler water will appear more concentrated than it really is. In any case the sample drawn out under pressure is usually a little stronger than the bulk of the water in the boiler.

The following examples will illustrate this. A sample of water was drawn very carefully from the bottom arm of the water gauge and was found to contain :—

Boiler Water (under pressure)

Carbonate of Lime	2.00
Caustic Soda	26.32
Carbonate of Soda	18.37
Nitrate of Sodium	42.84
Sulphate of Sodium	78.49
Chloride of Sodium	83.54
	<hr/>
	251.56
	<hr/>

This sample was taken whilst the boiler was still under 200 pressure, but pumping had been stopped for half an hour.

Another sample was taken from the blow-off cock of the same boiler after the pressure had fallen and showed zero on the pressure gauge. Temperature 212° F. when drawn off.

Boiler Water (after pressure had fallen)

Carbonate of Lime	75
Caustic Soda	17.92
Carbonate of Soda	9.62
Nitrate of Sodium	35.70
Sulphate of Sodium	79.84
Chloride of Sodium	59.79
	<hr/>
	203.62
	<hr/>

Another sample was taken from the bottom arm of the water gauge, when the pressure had fallen from 200 lb. to zero. This sample contained :—

Boiler Water (no pressure)

Carbonate of Lime	40
Caustic Soda	21.84
Carbonate of Soda	10.70
Nitrate of Sodium	35.70
Sulphate of Sodium	63.48
Chloride of Sodium	59.79
	<hr/>
	191.91
	<hr/>

As this sample of boiler water had come from the drum, and the drum was full of steam at 200 lb. pressure when shut down, this steam would condense in the drum and dilute the boiler water, hence this sample is slightly weaker than the sample drawn from the bottom of the boiler.

Taking the sample drawn from the blow-off under no pressure as the representative sample, then the sample drawn off under pressure was in this case 25 per cent. stronger than the bulk, and part of the water had evidently evaporated when the pressure was released. This point should not be overlooked in considering samples of boiler water drawn under pressure. It should also be borne in mind that if care is not taken to shut off the upper arm of the gauge glass the samples are liable to be weaker than the bulk, owing to condensed steam being mixed with the sample. If this precaution is not neglected then it may be taken that samples of water drawn from a boiler under pressure are likely to be slightly stronger than the water in the boiler.

To prevent the concentration getting too high, the boilers must either be emptied and refilled with fresh water or the blow-off cock must be used. By an intelligent use of the blow-off cock much hot water can be saved and the boilers worked much longer without emptying.

With a boiler working at 200 lb. pressure and using a coal of calorific value 12,000 B.T. Units at 20s. per ton, every thousand gallons of water unnecessarily blown away means a waste of 3s. 2d. over and above the value of the water itself.

CHAPTER VII

IRON

IRON is a very active metal and is readily soluble in acids. Sulphuric acid in a concentrated state does not dissolve it, but on dilution vigorously attacks it with the evolution of hydrogen. Iron also expels hydrogen from an aqueous solution of carbonic acid.

In perfectly dry air iron is not oxidized at ordinary temperatures, but in the presence of moist air it is rapidly oxidized and converted into rust. It takes away oxygen from carbonic acid and other organic acids and at high temperatures from water itself.

At a red heat iron burns in oxygen with the formation of a fused globule of the magnetic oxide Fe_3O_4 . In air iron absorbs oxygen at a red heat, forming the "scale" oxide. This is not a definite oxide but a mixture of ferric and ferrous oxides in variable proportions, generally containing about 80 per cent. iron and 20 per cent. oxygen.

Finely divided iron decomposes steam and water at 212°F. , forming the magnetic oxide and eliminating hydrogen. Finely divided iron prepared by heating ferrous oxalate out of contact with air, or by reducing ferric oxide with hydrogen at a low temperature, takes fire on exposure to air and burns to red ferric oxide. These properties are specially mentioned to show that iron is an easily oxidized metal, and will greedily pick up oxygen whenever it is placed in a position to do so.

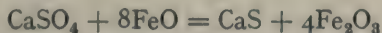
Iron as a metal is never used in the pure state, and it is at least doubtful whether pure iron has ever been obtained. Iron as we know it is really an alloy, the basis being metallic iron, in which is dissolved small quantities of other iron alloys, the principal of which are the alloys of iron and carbon, iron and silicon and iron and manganese. By varying the character and proportions of these alloys and by sometimes adding other alloys, the various forms of iron and steel used in commerce are

obtained, and each variety has its own distinct characteristic physical properties.

Iron forms three oxides, Ferrous oxide (FeO), Ferric oxide (Fe_2O_3), and Ferroso-ferric (magnetic) oxide (Fe_3O_4 or $\text{FeO} \cdot \text{Fe}_2\text{O}_3$).

Ferrous oxide is a black powder which readily absorbs oxygen from the air to form red ferric oxide. It can be prepared by reducing ferric oxide either with hydrogen or carbon monoxide at about 930°F. , or by heating metallic iron in carbon dioxide, to about the same temperature. In the one case oxygen is taken away from the ferric oxide by carbon monoxide forming ferrous oxide and carbonic acid, in the other metallic iron takes oxygen away from carbon dioxide forming ferrous oxide and carbon monoxide. Ferrous oxide is a powerful reducing agent and takes away oxygen from other bodies to form ferric oxide. Ferric oxide, on the other hand, when it is formed, somewhat readily parts with its oxygen to other bodies capable of taking it. Although metallic iron at a red heat takes away oxygen from carbonic acid, if air is blown into molten iron containing carbon, the carbon is oxidized before the iron, and if iron containing carbon is kept at a red heat for some time packed in ferric oxide, the ferric oxide oxidizes the carbon. Ferrous oxide dissolves in acids to form ferrous salts and forms a hydrate (FeOH_2O). Ferrous hydrate is a green gelatinous body which oxidizes so quickly on exposure to the atmosphere that extraordinary precautions have to be taken to prepare it. On exposure it rapidly turns to a rusty yellow powder consisting principally of ferric hydrate.

Ferrous hydrate is soluble in pure water to the extent of .5 grains per gallon. Ferrous hydrate when heated under pressure with sulphates reduces them to sulphides and forms ferric oxide. Thus:—



and



the base being set free and the water becomes alkaline.

Ferric Oxide is a reddish brown powder insoluble in water but soluble in most acids, forming yellow solutions of the respective ferric salts. The solutions of the ferric salts are more stable than the ferrous salts, as the iron is fully oxidized and can absorb no more oxygen. The ferrous salts can and do

absorb oxygen from the air and are therefore unstable. Under the influence of light and on great dilution the ferric salts do, however, undergo dissociation to a certain extent, and to this extent they may be considered unstable. Otherwise, under ordinary influences, they may be regarded as stable salts.

Ferric oxide unites with water in almost all proportions to form hydrates, and ferric hydrates containing variable quantities of water of hydration can be obtained by varying the temperature at which they are precipitated and the manner in which they are dried. Ferric hydrate may be said to have the composition $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$.

The hydrate obtained by precipitating a ferric salt with caustic soda or ammonia and drying it at 212°F . is a dark brown brittle mass having a fracture like cutch or gambier, and has the composition $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$. It is readily soluble in dilute hydrochloric acid, but if boiled for some hours in a large quantity of water it turns red in colour, becomes insoluble in dilute acids, and can only be dissolved by heating it with concentrated hydrochloric acid or sulphuric acid. The hydrates $2\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ are formed by boiling $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ for a long time with water. They are practically insoluble in cold dilute acids and have to be heated with strong acid to bring them into solution.

Under certain circumstances ferric oxide can be made to unite with strong bases to form a class of salts known as ferrites. In this case the ferric oxide plays the part of an acid. The ferrites are very unstable salts and are easily decomposed.

Ferroso-ferric oxide is probably a mixture of ferrous and ferric oxide, as when it dissolves in acids the result is a mixture of ferrous and ferric salts. From these solutions, however, the oxide can be reprecipitated and retains the same proportion of ferrous and ferric oxides. The solution can be oxidized, and when the oxidation is complete pure ferric hydrate can be precipitated. Short of complete oxidation the result of precipitation is the formation of a hydrate containing the ferrous and ferric oxides in a proportion dependent upon the amount of oxidation.

Ferroso-ferric oxide is a black magnetic powder although it is usually found in a partially fused condition coating the articles upon which it has been deposited. In this condition it does not rust, and forms a protective coating to the iron beneath it. This oxide has found some practical application as a protection from rust. The iron is first cleaned, then made nearly red hot

and submitted to the action of superheated steam. This is the "Barff" process, and articles coated in this way do not rust so long as the coating remains intact. Owing principally to the fact that the articles have to be heated to a high temperature and that the protecting coating chips off somewhat easily, this process has only found a somewhat limited application.

The hydrate $\text{Fe}_3\text{O}_4 \cdot x\text{H}_2\text{O}$ is produced by digesting ferric hydrate with metallic iron under water. This hydrate is probably one of the hydrates produced where rusting is going on in iron vessels with only a limited supply of air.

The hydrated oxides of iron vary in colour according to the method of preparation. The hydrate precipitated by an alkali from a ferric solution is dark brown, but the hydrate formed by oxidizing ferrous hydrate is of a yellowish ochrey colour. When the former hydrate is ignited to drive off the water of hydration, it remains brown, but the yellow oxidized hydrate turns bright red on ignition. The ferric and ferrous hydrates readily change from one to another. Ferric hydrate is reduced to ferrous hydrate by contact with metallic iron, and ferrous hydrate is converted into ferric hydrate by contact with air. Ferrous oxide or hydrate also takes away oxygen from many substances containing it, such as permanganate of potash, carbonic acid, etc. When the reduction of the ferric oxide or the oxidation of the ferrous oxide is not complete it is possible to obtain a mixture of these oxides or hydrates in almost any proportion.

Iron forms three sulphides corresponding to the oxides.

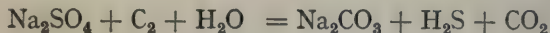
Ferrous Sulphide (FeS) is a fusible metallic-looking, brown brittle substance, easily prepared by heating iron and sulphur together, also by burning iron wire in sulphur vapour, and is formed whenever sulphur is heated in contact with metallic iron.

A hydrated sulphide is formed as a dark green precipitate when alkaline sulphides are brought into contact with ferrous salts in solution. On exposure to air, ferric hydrate is formed and sulphur separates in the free state. This reaction is made use of in the purification of coal gas. The crude gas containing sulphuretted hydrogen is passed through large boxes containing moist ferric hydrate mixed with sawdust to render it porous. The sulphuretted hydrogen is absorbed, ferrous sulphide and water being formed. When the oxide no longer purifies the gas sufficiently, air is passed in—or the boxes are opened and the contents spread out in thin layers on the ground, so as to expose it to the air. Oxygen is absorbed, ferric hydrate is

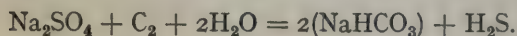
reformed and sulphur separated. When the action is complete the current of air is stopped or the mixture is put back into the boxes and purification proceeds as before. The process is repeated over and over again until the oxide contains 40-50 per cent. of free sulphur, when it is sold to the sulphuric acid manufacturers as spent oxide and used for making sulphuric acid.

If gas containing sulphuretted hydrogen is burnt in a furnace in insufficient air, and the jet impinges on iron tubes or plates, part of the sulphur unites with the iron to form the readily fusible sulphide of iron, and the metal is weakened and destroyed.

Ferrous sulphide is also produced in stagnant waters by the reduction of sulphates by organic matter, in contact with oxide of iron. Sulphates are also reduced by organic matter without the assistance of oxide of iron, and samples of water from hot climates often contain traces of sulphuretted hydrogen on arrival in this country, although they contained no sulphuretted hydrogen when bottled up. The fact should be noted when estimating the amount of sulphates and carbonates in such samples. The sulphates will be less in the samples at this end than they were at the place of origin and the carbonates higher, thus :—



or



Another form of sulphide of iron is the disulphide FeS_2 , which occurs in Nature as iron pyrites. Iron pyrites is often found in coal, and the sulphur in coal is generally pyritic, though coal does contain sulphur in other forms. When burnt it is converted into sulphurous acid and ferric oxide, and where there is excess of air the sulphurous acid is more or less converted into sulphuric acid.

RUSTING

Iron is a metal nearly always existing in Nature as an oxide or hydrate, and a great amount of heat energy has to be used to separate it from its oxygen and bring it into a form suitable for industrial uses. Hence iron is always striving to get back this oxygen and to again become oxide of iron. Copper, on the other hand, exists generally as a sulphide and only occasionally as an oxide, and as the atmosphere is practically free from

sulphur, copper under ordinary influences is a less corrodible metal than iron.

The coating of ferric oxide which forms on rusting surfaces of iron has the property of transferring oxygen to the iron, becoming reduced itself to ferrous oxide in the process. This ferrous oxide being easily reoxidized, the coating of rust acts as a carrier of the oxygen from the atmosphere to the metallic iron, and the metal in time becomes rusted right through.

There are two principal theories to account for corrosion or rusting. The one theory is that carbonic acid is the active agent in the corrosive process, the other that *pure* water is an electrolyte and that the dissimilar particles of the iron act as cathodes and anodes and set up an electrolytic action whereby certain parts are converted into oxide of iron and other parts give off hydrogen. As it is not possible to obtain pure water any more than it is possible to obtain pure iron, it cannot be proved or disproved that pure water *per se* is an electrolyte; and if the theory has to rely on carbonic acid derived from the atmosphere, then the electrolytic theory becomes merged into the carbonic acid theory. No doubt there is some electrolytic action in the corrosion of iron, but the carbonic acid is more probably the electrolyte than the water itself. In the absence of carbonic acid iron does not rust, and it is therefore only reasonable to suppose that carbonic acid is the determining cause. On the other hand, carbon dioxide in the absence of water does not corrode iron at ordinary temperatures. This is most probably due to the fact that carbon dioxide in itself is not an acid (although it is commonly called carbonic acid), and only becomes an acid by uniting with an equivalent quantity of water. Dry carbon dioxide does not affect dry litmus paper, but when water is brought into the process blue litmus is turned red, one proof of the formation of an acid. As no ordinary case of rusting or corrosion has been shown to take place in the absence of some acid, the carbonic acid explanation seems the most reasonable, and the electrolytic theory is more an academic discussion than an explanation of the process of corrosion.

COMPOSITION OF RUST

Iron wire (piano wire) was put into cylinders containing a soft water and loosely covered. The cylinders were allowed to stand for five years, during which time the water evaporated,

and for about two years there was no water left in the vessels. At the end of five years the wires were taken out and found to be rusted right through, and in many cases there was no wire left. This rust was collected and was found to have the following composition :—

Silica	3.02
Ferrous Oxide	4.32
Ferric Oxide	79.68
Water of Hydration	10.16
Soda, etc. (diff.)	2.82
	<hr/>
	100.00
	<hr/>

The silica and the soda were derived from the glass vessels in which the wires were suspended. If these are eliminated from the analysis and the analysis recalculated without them, the rust would have the following composition :—

Ferrous Oxide	4.59
Ferric Oxide	84.62
Water of Hydration	10.79
	<hr/>
	100.00
	<hr/>

Another sample of rust obtained by agitating powdered iron in water containing carbon dioxide and oxygen consisted of :—

Ferrous Oxide	5.59
Ferric Oxide	84.14
Water of Hydration	10.11
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	99.84
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Another sample was prepared by agitating ferrous oxide with air in presence of a little caustic soda, so that the caustic soda should absorb any carbon dioxide in the air and only oxygen should be left to carry on the oxidation. This sample had the following composition :—

Ferrous Oxide	7.63
Ferric Oxide	83.54
Water of Hydration	8.80
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	99.97
	<hr/>

All these samples were air-dried at a temperature of 60°–70° F.

Another sample was prepared by agitating ferrous oxide with

water and air until the ferrous oxide had been completely converted into ferric oxide. Analysis showed it to contain :—

Ferric Oxide	89.12
Water of Hydration	11.00
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	100.12
	<hr/>

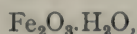
A sample of rust taken from a pipe through which cold water had been passed for some years contained :—

Silica42
Ferrous Oxide	5.18
Ferric Oxide	73.28
Water of Hydration	20.40
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	99.28
	<hr/>

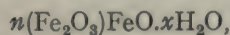
Another sample from a cold water pipe :—

Silica40
Ferrous Oxide	17.28
Ferric Oxide	72.08
Water of Hydration	10.24
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	100.00
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From these examples it will be seen that rust is a variable mixture of ferrous and ferric oxide, with a certain amount of water of hydration, which is largely dependent upon the temperature at which the rusting has taken place. The average percentage of the oxides of iron is 80-90 per cent. and the water of hydration 20-10 per cent.; when the iron is fully rusted the composition would be approximately Ferric Oxide 90 per cent., Water of Hydration 10 per cent., which gives a chemical formula approximating very closely to :—



but when not fully oxidized and kept quite cold, as it would be in a cold water service, the formula would be :—



but in any case rust is hydrated oxide of iron, and contains nothing else than iron, oxygen and water.

The colour of rust is no criterion of its richness in oxygen, the shade of yellow depending more upon its percentage of water of hydration than upon the percentage of oxygen.

All the foregoing are examples of rust formed in the cold. In feed pipes and economizer tubes in which the temperature of

the water is anything between 140° – 210° F. rust or corrosion deposits are formed which are only distinguished from ordinary rust by their colour, which is generally a dark rich red, although they often contain as much ferrous oxide and as much water of hydration as the yellow rusts.

The following are analyses of samples taken from Economizers in which corrosion had been going on :—

Silica	3.21
Ferrous Oxide	5.76
Ferric Oxide	81.92
Oil	2.58
Water of Hydration	5.50
	<hr/>
	98.97
	<hr/>

Silica26
Ferrous Oxide	8.64
Ferric Oxide	89.12
Water of Hydration	1.98
	<hr/>
	100.00
	<hr/>

Silica34
Ferrous Oxide	17.86
Ferric Oxide	73.88
Zinc Oxide	2.65
Oil	2.10
Water of Hydration	2.48
	<hr/>
	99.31
	<hr/>

This tube had been galvanized :—

Silica and Graphite	15.36
Ferrous Oxide	28.80
Ferric Oxide	36.80
Sulphuric Anhydride	1.29
Phosphoric Anhydride	1.38
Water of Hydration	16.37
	<hr/>
	100.00
	<hr/>

This deposit is from cast iron :—

Silica	5.55
Graphite	4.25
Ferrous Oxide	15.84
Ferric Oxide	63.28
Sulphuric Anhydride60
Phosphoric Anhydride	3.38
Water of Hydration	6.88
	<hr/>
	99.78
	<hr/>

This is also from cast iron. If the silica, graphite, etc., are eliminated as impurities and the analysis recalculated on a basis of 100 per cent. without them, the composition would be :—

Ferrous Oxide	18.42
Ferric Oxide	73.58
Water of Hydration	8.00
	<hr/>
	100.00
	<hr/>

Cast-iron water pipe buried in the ground :—

Silica	14.88
Alumina	9.55
Graphite	4.56
Ferrous Oxide	47.49
Ferric Oxide	4.82
Water of Hydration	18.70
	<hr/>
	100.00
	<hr/>

Eliminating the Silica and Alumina as being clay on the outside, the analysis would be :—

Graphite	6.39
Ferrous Oxide	62.83
Ferric Oxide	6.03
Water of Hydration	24.75
	<hr/>
	100.00
	<hr/>

CHAPTER VIII

CARBONIC ACID

CARBON dioxide, or, as it is commonly called, carbonic acid, exists in the atmosphere to the extent of about 4 parts in 10,000 or .04 per cent. by volume, and any quantity in excess of this is prejudicial to human life. Carbonic acid does not burn, as it is carbon in its maximum state of oxidation, and as it does not readily part with any of its oxygen it will not support ordinary combustion. Nevertheless it can be made to give up part of its oxygen to certain metals, and altogether is not such a stable body as is generally imagined.

It is produced by the oxidation of bodies containing carbon and plays a very important part in all organic life. Animals continually exhale it and add it to the atmosphere, and were it not for a certain provision of Nature, the atmosphere would soon become so polluted with it as to render it inimical to animal life. The green part of plants under the influence of sunshine and moisture have the power of absorbing this carbon dioxide, disintegrating it, retaining its carbon and restoring much of its oxygen to the atmosphere. This plant action is endothermic, the heat absorbed is rendered latent in the plant and is released again when the plant is burnt either as wood, peat or coal.

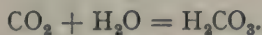
In past ages, woody fibre or cellulose formed in this way has been buried, converted first into peat, then lignite, bituminous coal, and finally into anthracite, which is nearly pure carbon. The process of lignification seems to be a very gradual elimination of the hydrogen and oxygen with a little carbon, the result being that it becomes relatively richer in carbon. The carbon which is thrown off in combination with the oxygen and hydrogen often forms those organic acids found in peaty waters. In many cases these acids are exceedingly complicated bodies such as ulmic acid ($C_{18}H_{14}O_6$), or crenic acid ($C_{12}H_{12}O_8$), in other cases the acid formed is a simple body such as glycollic acid ($C_2H_4O_3$) or

formic acid (CH_2O_2). Whether this disintegration of the peat is due to bacterial action or not, need not be discussed here, it being sufficient for the purpose to note that the oxidation of the peat yields organic acids which get into the water and can become fruitful sources of corrosion in boilers.

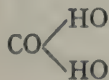
Rain-water as it reaches the ground seldom contains more than half a grain of carbonic acid per gallon, but even this quantity in combination with the oxygen which is also dissolved is a most powerful disintegrating agent, and no rocks are able to resist its solvent action. It is Nature's solvent, by means of which rock masses are disintegrated, the soluble matters being removed by the water and the insoluble residue, consisting principally of silica and alumina, spread out to form the soil covering the arable parts of the earth's surface.

Carbonic acid is a colourless gas having a density of 1.53 compared with air, and is slightly soluble in water. Water at 60°F . dissolves its own volume of carbonic acid, hence 1 gallon of water at 60°F . dissolves approximately 4500 c.c. of carbonic acid gas. This solution of carbonic acid is a true acid and affects litmus and other indicators. Metals such as iron, zinc and magnesium expel hydrogen from the solution and a carbonate of the metal is formed.

Carbonic acid may be considered to be the acid formed when carbon dioxide unites with the elements of water in exactly the same way as sulphur trioxide unites with water to form sulphuric acid :—

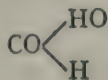


Graphically H_2CO_3 or CH_2O_3 may be represented thus :—

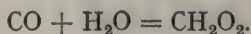


Carbonic acid therefore contains the group $\text{CO}-\text{HO}$ and comes into line as an organic acid containing the carboxyl group.

If one of the Hydroxyl groups (HO) is replaced by Hydrogen (H) a very common reaction in organic chemistry, the carbonic acid becomes



which is formic acid CH_2O_2 , and this acid still retains the Carboxyl group $\text{CO}-\text{HO}$. Formic acid may also be considered to be the acid formed when carbon monoxide unites with water thus :—



When both the hydroxyl groups are replaced by hydrogen the formula becomes



This substance does not contain the group $\text{CO}-\text{HO}$, and is therefore not an acid. It is, in fact, formaldehyde (CH_2O), and the three bodies are in direct relation.

$\text{CO}-(\text{HO})_2$ or CH_2O_3 carbonic acid

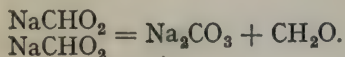
$\text{CO}-\text{HO}-\text{H}$ or CH_2O_2 formic acid

$\text{CO}-\text{H}-\text{H}$ or CH_2O formaldehyde,

and these bodies only differ in composition by containing different amounts of oxygen.

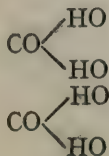
If, then, one atom of oxygen be removed from carbonic acid, formic acid should be formed. This can be done by means of iron, for when iron is sealed up with carbonic acid and left for some time, formic acid is formed and ferrous oxide goes into solution.

Formaldehyde can be prepared by heating formate of soda to $300^\circ-400^\circ \text{F.}$, thus :—

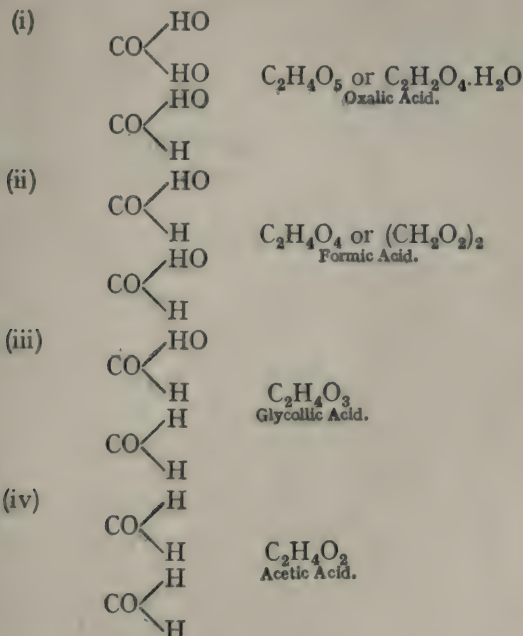


Thus carbonic acid is reformed and the other half of the carbon goes off as formaldehyde.

Two molecules of carbonic acid can be graphically represented thus :—



If the (HO) groups are successively replaced by hydrogen, the following formula are obtained :—



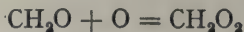
On the basis of two molecules of carbonic acid these acids form a series, each one differing from the one above it by containing one atom of oxygen less.

Carbonic Acid	$\text{C}_2\text{H}_4\text{O}_6$ or 246 acid.
Oxalic Acid	$\text{C}_2\text{H}_4\text{O}_5$ „ 245 „
Formic Acid	$\text{C}_2\text{H}_4\text{O}_4$ „ 244 „
Glycollic Acid	$\text{C}_2\text{H}_4\text{O}_3$ „ 243 „
Acetic Acid	$\text{C}_2\text{H}_4\text{O}_2$ „ 242 „

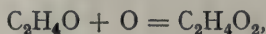
and if one more atom of oxygen is removed from acetic acid, the product cannot contain the carboxyl group $\text{CO}-\text{HO}$, and cannot therefore be an acid. By removing one atom of oxygen the product is acetic aldehyde ($\text{C}_2\text{H}_4\text{O}$), and if the last atom of oxygen is removed the final product is C_2H_4 Ethylene or olefiant gas.

These aldehydes are volatile bodies, easily driven off by heat from their solutions in water, they do not unite with bases to form salts in the same way as the acids.

Formaldehyde is easily oxidized to formic acid



and acetaldehyde to acetic acid

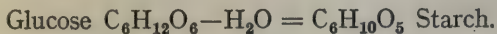


and Ethylene (Olefiant gas) can be easily transformed into acetic, glycollic, formic, oxalic and carbonic acids by suitable oxidizing agents.

In this series of acids, the first two, viz. carbonic and oxalic, are dibasic acids, and the other three, formic, glycollic and acetic are monobasic acids. Only oxalic and carbonic acid form any insoluble salts, all the salts of the other acids are soluble.

The aldehydes possess the somewhat remarkable property of polymerizing, that is to say, several molecules group themselves together to form solid products having the formula $n(\text{CH}_2\text{O})$ or $n(\text{C}_2\text{H}_4\text{O})$. These polymerized aldehydes have the further property of condensing first into more complicated aldehydes, and these again condense to other bodies analogous to, if not identical with the carbohydrates, sugars, starches, resins and celluloses.

Formaldehyde (CH_2O) in contact with lime or magnesia condenses to formose ($\text{C}_6\text{H}_{12}\text{O}_6$) or $6(\text{CH}_2\text{O})$. Formose is undoubtedly a body possessing most of the characters of a sugar, and is certainly a carbohydrate as it gives many of the chemical reactions of the starches and sugars. The chemical formula of the sugars only differs from the formula of the starches in the elements of water. Thus:—



Thus starch by taking up one molecule of water is converted into sugar. Glucose is manufactured commercially by heating starch with dilute acid. The starches apparently possess the property of further condensation to such bodies as Inulin $n(\text{C}_6\text{H}_{10}\text{O}_5)$ and Cellulose $n(\text{C}_6\text{H}_{10}\text{O}_5)$, the chemical formula of which probably only differ in the value of n .

The accompanying diagram represents these changes in a graphic form. The upper curve shows the fall in the percentage of oxygen and the lower the upward tendency of the carbon. In two places the curve is stationary and marks the point at which polymerization or condensation takes place without any

alteration in the relative percentages. After the first break another fall and corresponding rise takes place and the curve is again stationary where the condensation of the carbohydrates into cellulose takes place.

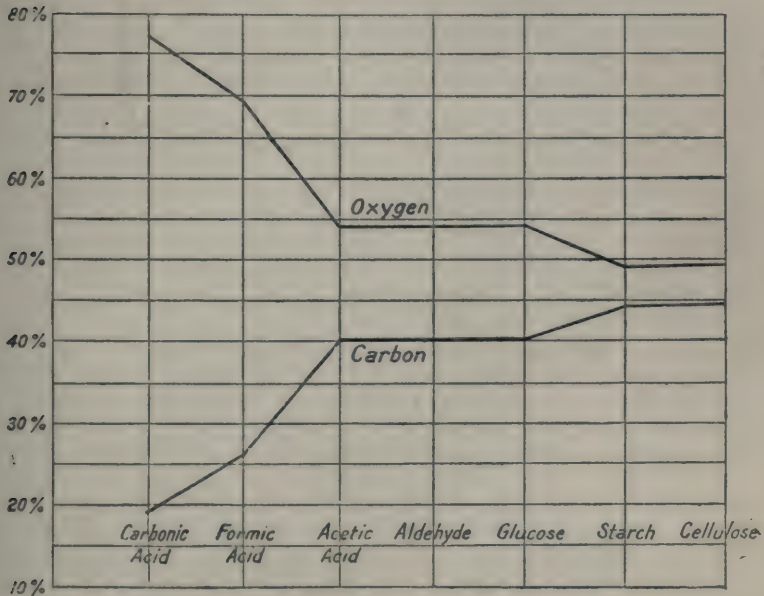


DIAGRAM 19.

The actual percentages as represented by the curves are:—

	Oxygen, per cent.	Carbon, per cent.
Carbonic Acid	77.42	19.35
Formic Acid	69.57	26.09
Acetic Acid	53.33	40.00
Formaldehyde	53.33	40.00
Glucose	53.33	40.00
Starch	49.38	44.44
Cellulose	49.38	44.44

All these bodies from cellulose upwards are products of the assimilation of carbonic acid by plant life. The reactions which take place, whether biological or chemical or both, are characterized by the disappearance of carbonic acid and the appearance of free oxygen, and when the oxygen is fully restored to any of these bodies, carbonic acid is again produced. By

limiting the amount of oxygen supplied to some of these bodies or by removing oxygen from others, nearly all these bodies can be converted from one into the other, and all of them can, with the possible exception of inulin and cellulose, be built up synthetically from carbonic acid and water without the intervention of plant life. Starting with carbonic acid it is therefore possible to produce first formic acid, then formaldehyde, and then sugar, and it is possible to reconvert the sugar, formaldehyde and formic acid back again into carbonic acid.

Having traced some of the transformations which can take place when carbonic acid has been deprived of more or less of its oxygen, the next question is whether any of these reactions take place in the boiler.

CHAPTER IX

CONCENTRATION OF WATERS CONTAINING CARBONATE OF SODA

WHEN waters containing carbonate of soda are concentrated in boilers working at 100 lb. pressure and upwards, a portion at least of the carbonate of soda is converted into caustic soda, and as the pressure rises towards 200 lb. per sq. inch the conversion is more pronounced, and in many cases it is not at all unusual to find that this conversion is quite complete and that the whole of the carbonate has become converted into caustic.

At a red heat carbonate of soda melts without decomposition, that is, without losing any of its carbonic acid, but if the carbonate of soda is heated to a red heat in a current of superheated steam it readily loses its carbonic acid and is converted into caustic soda. As a red heat may be taken at about 1400° F., it is evident that nothing like this temperature is obtained in the boiler water, so that it is not at all likely that the decomposition is merely a splitting up of the carbonate into its constituents, viz. sodium oxide and carbonic acid (the sodium oxide in the presence of water forming caustic soda).

If this were so, the carbonic acid in the case of condensing engines would accumulate in the condensed water which is returned over and over again to the boilers. Water at normal temperatures dissolves about its own bulk of carbonic acid gas, therefore each gallon of such condensed water should be able to dissolve something like 4500 c.c. of the gas, but in point of fact out of several hundred samples of condensed water examined not one contained more than 100 c.c. of carbonic acid, and experience shows that 100 c.c. is rather a high figure for condensed waters, unless they are contaminated with outside condensing water owing to leaky condensers.

The argument that being a gas it escapes from the "condensing cycle" with the air from the air-pump discharge, does not hold good for two reasons: (1) the condensed water is found to be always nearly saturated with free oxygen, and this gas is very much less soluble in water than carbonic acid, and (2) that

carbonic acid gas up to the point of saturation forms a chemical compound with the water, from which the gas is not readily liberated, until the saturation point is reached, which, as before mentioned, would be about 4500 c.c. for water at 60° F.

Four facts therefore require to be carefully noted :—

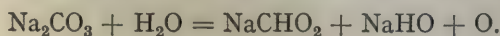
- (1) The destruction, partial or total, of the carbonate of soda.
- (2) The disappearance, partial or total, of the carbonic acid.
- (3) The appearance of caustic soda.
- (4) The constant presence of oxygen in quantity sufficient to keep the condensed water nearly or quite saturated and also to escape with the gases from the air pump. In fact, if the temperature of the Hot Well is considered to be fairly constant at 100° F. to 110° F. the condensed waters must sometimes be supersaturated with oxygen. This, to say the least, is peculiar, as the water has been condensed in a vacuum.

The presence of free oxygen may be ascribed to the make-up water which is often quite saturated with this gas, but as in many cases the make-up is only 3 per cent. of the condensate and the condensate is always nearly or quite saturated, and in addition there is always an escape of air or gas containing oxygen, it appears more than probable that oxygen is a result of the disintegration of the carbonate of soda.

The appearance of oxygen taken in conjunction with the disappearance of carbonic acid, and at the same time the formation of caustic soda, would point to a regrouping of the carbon and oxygen atoms. Carbonic acid is a group in which 1 carbon atom is associated with 2 atoms of oxygen, and is what is called a divalent radicle, that is, it requires 2 atoms of a metal such as sodium to satisfy it. On the other hand, the group formed by the association of 1 atom of carbon with 1 atom of oxygen is monovalent and only requires 1 atom of sodium to satisfy it.

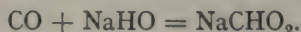
Hence, if this destruction of the carbonate is brought about by a regrouping of the carbon and oxygen atoms, the disappearance of the carbonic acid would mean the appearance of oxygen and at the same time the setting free of half the metal of the carbonate, that is, the formation of 1 molecule of caustic soda for every molecule of carbonate of soda decomposed.

This might be represented by the following equation :—



This will account for the disappearance of the carbonate, and the appearance of caustic soda and free oxygen. At the same time

the carbon has regrouped itself into the combination NaCHO_2 which is *formate of soda*. Formate of soda is the salt formed when carbon monoxide combines with caustic soda. Thus :—



Thus a salt has been formed in which the carbon is associated with only 1 atom of oxygen instead of 2, as in the case of the carbonate.

If this reaction has really taken place, the carbonate water which originally did not destroy permanganate of potash should destroy this salt, as the formates are strong reducing agents. In point of fact nearly all boiler waters do reduce the permanganate considerably. This has hitherto been ascribed to organic matter in the original waters, but as formic acid is an organic acid, it may be that some at least of this reducing power is due to formates or carbohydrates produced in this way.

In order to throw some light on the subject the following research was undertaken.

A boiler water was obtained which had been formed by concentrating an artesian well-water at a pressure of 150 lb. per sq. inch. This well-water was a carbonate of soda water and practically free from organic matter. The analysis of this boiler water was as follows :—

Boiler Water

Silicate of Soda	6.25
Caustic Soda	179.26
Carbonate of Soda	204.05
Sulphate of Soda	19.80
Chloride of Sodium	291.56
	<hr/>
	700.92
	<hr/>

According to this analysis the total solids amounted to 700.92 grains per gallon, but on evaporating some of the water to dryness and heating it to about 230° F. the total solids amounted to 826 grains. As, however, the caustic soda on evaporation in air picks up carbonic acid and does not part with the whole of the water, this result is too high. To get over this difficulty, the water was treated with a sufficient quantity of carbonic acid, so that all the caustic soda was converted into carbonate. The water was then evaporated to dryness and dried at 230° F., when the total solids were found to be 802.48.

If the caustic soda given in the analysis is calculated into

carbonate, this would make the total solids 765.03 grains, so that there is the difference of $802.48 - 765.03 = 37.45$ grains to be accounted for.

The amount of sodium oxide was then carefully determined and found to be 434 grains per gallon. This amount of sodium oxide could not be all accounted for by calculating the sodium oxide equivalents of each of the constituents. The accompanying balance sheet show 9.4 grains unaccounted for.

Soda Balance Sheet

DR.	Grains.	CR.	Grains.
Sodium Oxide found	434	Sodium Oxide corresponding to	
		Sodium Silicate	3.19
		„ Caustic	138.92
		„ Carbonate	119.35
		„ Sulphate	8.64
		„ Chloride	154.50
		Balance unaccounted for	9.40
	<u>434.00</u>		<u>434.00</u>

As both these results show that there is something else in the water it was decided to look for another acid in the following way.

Half a litre of the water was carefully neutralized with sulphuric acid to destroy the carbonates, and then treated with sulphate of silver to remove the chlorides, in case any volatile hydrochloric acid would come over when the water was afterwards distilled.

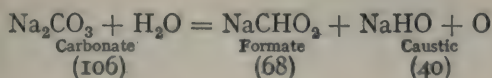
The water filtered from the chloride of silver was treated with a slight excess of phosphoric acid and distilled.

The first 100 c.c. of the distillate was rejected in case it might contain some carbonic acid.

The remaining portion of the distillate was found to be acid, and required 5 c.c. N/10 Caustic Potash to neutralize it, phenolphthalein being used as the indicator.

It was further found that the distillate decolorized permanganate of potash. No precipitate was formed with nitrate of silver, but only a brown coloration, such as is obtained when weak solutions of formic acid are boiled with silver salts. As care had been taken to remove any chlorides before distillation with phosphoric acid, the only acid which could distil over from this water would be an organic acid which did not form an insoluble silver salt. The destruction of some permanganate showed that some of this acid at least must have been formic

acid, though some of it might have been acetic acid, and it can hardly be doubted that this boiler water did contain some formate of soda. Once this fact is established the caustic soda is accounted for, as well as the free oxygen always found in the steam, and the reaction which takes place is explained by the equation:—



Although this equation will explain the formation of formate of soda and caustic soda the reaction must go further than this, otherwise the amount of formate of soda (68) should always be greater than the amount of caustic soda (40), but the balance sheet shows that the amount of sodium oxide in the formate could not possibly have exceeded 9·4 grains, whereas the sodium oxide in the caustic soda amounted to 139 grains, and this is confirmed by the relatively small amount of volatile organic acid obtained by the distillation with phosphoric acid. It is therefore evident that the reaction does not stop with the production of formic acid, and that the formic acid in its turn must be decomposed. The boiler water referred to, and which has just been dealt with, was taken from a boiler working at 150 lb. pressure and fed with a water consisting of equal proportions of a soda well-water and condensed steam from the same boiler, so another investigation was made on a water taken from a boiler working at 200 lb. pressure, and evaporating a carbonate of soda water without any dilution whatever.

The analysis of the boiler water showed it to contain:—

Boiler Water

Nitrate of Sodium	5·95
Sulphate of Sodium	383·38
Caustic Soda	127·12
Carbonate of Sodium	117·24
Chloride of Sodium	389·02
	<hr/>
	1022·71
	<hr/>

The soda balance sheet was made out as in the previous case, and as the difference unaccounted for was only 1·98 grains per gallon, it was thought that for the purpose of this investigation it might be considered to be negligible.

Another portion was evaporated to dryness with an excess

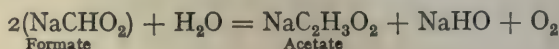
of carbonic acid to convert all the caustic soda into carbonate, then dried at about 230° F. until it ceased to lose weight. The weight after deducting the amount of carbon dioxide which would have been taken up, was found to be 1075.96 grains per gallon as against 1022.71 grains found by adding up the constituents, a difference of 53.25 grains. When the residue was heated it blackened slightly and after gentle ignition the loss was found to amount to 51.52 grains per gallon, which is very nearly the actual difference between the weight found and that calculated by adding up the constituents.

It was also found that the dry residue was insoluble in ether, but that strong alcohol dissolved up an amount equal to 15.84 grains per gallon, and that although no Fehling Solution was decolorized, the colour of a considerable amount of permanganate of potash was discharged. Time did not permit of a further examination of the residue, but it is hoped to return to the subject on a future occasion. Sufficient evidence, however, has been gathered to show that the formate, which the previous investigation has shown to be formed, has been further decomposed and that the organic acid has become separated from the soda and become condensed to an organic body having some of the characteristics of the carbohydrates.

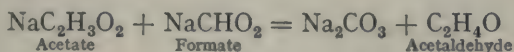
Other samples of these carbonate of soda boiler waters show that whereas there is often a considerable amount of these organic salts present, the quantity diminishes as concentration proceeds, and sometimes the water turns quite brown, probably being coloured by some sugary body resembling caramel.

It is found that in some cases the ratio of the carbonate of soda to the caustic, which at first falls, after a time begins to rise again, and instead of the amount of caustic soda increasing as concentration goes on, it actually decreases while the carbonate increases, and in some boiler waters the ratio is continually chopping and changing. This points to some reversible reactions which are evidently going on, by means of which some of the caustic soda is reconverted into carbonate.

Having established the fact that formate of soda is one of the products in these reactions, the next point is to examine the reactions which may occur when formate of soda is heated to about 400° F. with caustic soda under pressure. One of the reactions is the formation of acetate of soda, thus :—



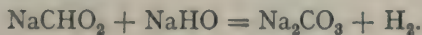
This being a further step in the process of degradation oxygen is still eliminated. Any further step in the degradation must be the formation of an organic salt containing less than 2 atoms of oxygen, seeing that the formula for the acetate is $\text{NaC}_2\text{H}_3\text{O}_2$. And if it only contains 1 atom of oxygen it cannot contain the group $\text{CO}-\text{HO}$, and therefore cannot be an organic acid. Any further step must perforce give rise to a body which must separate from the soda, and either remain in solution as a separate body or be given off with the steam. A probable reaction is the following :—



In this case acetaldehyde is set free and carbonate of soda reformed, and this will help to explain why the ratio of the carbonate to the caustic soda in boiler waters is continually changing, although the total alkalinity is always increasing as the concentration proceeds.

Aldehyde is a volatile body and no doubt some of it escapes with the steam, but, as already mentioned, the aldehydes have the property of polymerizing and condensing into bodies of the carbohydrate class. A portion of the aldehyde will thus be transformed into a sugary or resinous body and remain in the boiler water. Another reaction will then take place, for as the caustic soda solution gets concentrated it will in its turn attack these bodies, forming numerous products, amongst which may be mentioned acetone, lactic acid, and perhaps the hydrocarbons themselves.

Another reaction which may occur in boilers working with these waters at 200 lb. pressure and above, is the setting free of hydrogen and reformation of carbonate :—



The formate and caustic react upon one another to reform carbonate and set free hydrogen.

From these instances it is seen that a numerous and complicated series of reactions take place, some of which are reversible; carbonic acid at one time being decomposed and at others being reformed, the ultimate result being the formation of caustic soda, and the conversion of some of the carbonic acid into volatile products and some into products which remain in the boiler.

Although the whole question is exceedingly complicated and interesting and many other reactions no doubt take place, the most important point is how far these reactions affect the steam.

Condensed steam from boilers working under these conditions never contains more than a trace of carbonic acid, and it is extremely doubtful whether this trace is carbonic acid at all. The methods of analysis adopted for estimating free carbonic acid in waters would equally well estimate any other acid which could be present, and it is probable that the minute quantity of acid present in condensed steam is not carbonic acid at all, but formic acid, and in some cases it may be glycollic or even lactic acid. Some condensed waters which are slightly acid leave a small quantity of solid residue when evaporated. This acid residue is sometimes left as a gummy mass, which blackens on heating, and burns completely away when ignited. Formic acid would leave no residue, but would be expelled with the steam during evaporation.

Even when the steam has left the steam drum it has still to run the gauntlet of the superheater, where it is raised to a still higher temperature. Any further heating of the volatile bodies in the superheated steam and in presence of iron will cause another series of reactions, so that if carbonic acid did actually leave the boiler water it would still run a very poor chance of escaping as such. A modern high-pressure boiler is a chemical factory in which innumerable complicated reactions take place, and many different products are formed. That an alkaline boiler water containing carbonate of soda should develop acid is at first sight somewhat startling, but the evidence that the carbonate of soda is broken up in the way described and the acid developed is overwhelming.

The best way of getting over this difficulty with carbonate of soda is, if possible, to prevent it getting into the boilers at all. As a soda alkalinity is necessary to prevent corrosion in the boilers, the soda should go into the boilers as caustic soda. This can be carried out by treating the make-up water with an excess of calcium hydrate in addition to the soda. This excess need be very slight, and it fulfils the double purpose of destroying all the carbonate of soda, and keeping a slight excess of calcium hydrate in the boiler water. If at any time, through variation in treatment or other cause, carbonate of soda did get into the boiler, the calcium hydrate already there would convert it into caustic, and remove the carbonic acid as carbonate of lime, in which state it is inert.

Carbonate of lime, unlike carbonate of soda, is not broken up in the boiler water, and for this reason it is an advantage to have a little free lime in the boilers. This free lime will in course of time form a scale, but the quantity used need be so small that only a very thin scale will be formed and the boilers can be run a long time without cleaning.

By adopting this method the steam is quite free from any trace of acid and does not attack the economizers and feed pipes. The following are tests of two samples of condensed steam from the same boiler, (1) when corrosion was taking place, and (2) when corrosion in the economizers had been arrested by the above-mentioned method.

Condensed Steam No. 1

Mineral Residue	nil
Organic Residue112 grains per gall.
Reaction, <i>acid</i> to Azolitmin and Rosolic Acid :—		
Acid calculated as Carbonic Acid		.462
Free Oxygen	31.05 c.c. per gall.

The sample decolorized a small quantity of permanganate of potash and gave a straw-coloured solution on boiling with nitrate of silver.

Condensed Steam No. 2

Mineral Residue	nil
Organic Residue	nil
Reaction, <i>neutral</i> to Azolitmin and Rosolic Acid :—		
Free Acid	nil
Free Oxygen	28.57 c.c. per gall.

The sample gave no coloration when boiled with nitrate of silver, nor did it decolorize permanganate.

CHAPTER X

ACTION OF CARBONIC ACID ON IRON

It has already been shown that in the boiler carbonic acid passes successively through certain phases of degradation, at the high temperature and pressure to which it is subjected. In this chapter it will be shown that metallic iron at ordinary temperatures can produce the same series of reactions, and that the oxidation of the iron takes place at the expense of the carbonic acid, which is reduced, first to formic or acetic acid and afterwards to aldehyde.

Distilled water was boiled to drive off oxygen, then shaken up with carbonic acid gas until it contained 21.2 grains of free carbonic acid per gallon.

This solution was shaken up with finely powdered iron, covered up, and then allowed to stand for 24 hours. At the end of that time the solution was tested, with the following results:—

	Grains per Gallon.
Ferrous Oxide in solution determined by weight	27.72
" " " " " by Permanganate	30.24

Another experiment was made in which a stream of carbonic acid was passed through the solution for half an hour, the levigated iron being kept in suspension all the time by means of a turbine stirrer. The mixture was then covered up and set aside for 24 hours. At the end of that time the clear solution was again tested with the following result:—

	Grains per Gallon.
Ferrous Oxide by weight	78.12
" " by Permanganate	80.64

It is therefore evident that in 24 hours a very noticeable quantity of iron goes into solution in carbonic acid. It was then decided to get some idea of the time required to get the iron into solution, and the following experiment was carried out

with this purpose in view. Recently boiled and cooled distilled water and levigated iron were agitated by a turbine stirrer for 30 minutes in a continuous stream of carbonic acid gas. The clear solution showed exactly the same amounts of ferrous oxide as in the last experiment, viz.:—

	Grains per Gallon.
Ferrous Oxide by weight	78·12
" " by Permanganate	80·64

The current of carbonic acid was then stopped, but the agitation was continued for 8 hours longer. At the end of that time there was no iron in solution and the carbonic acid had entirely disappeared.

The iron during the agitation first turned green, then yellowish, and the final product was principally ferric hydrate, no carbonate or oxalate could be detected, and the solution contained nothing which destroyed permanganate. In order to confirm this action, another experiment was made as follows. A solution of carbonic acid in recently boiled distilled water was agitated with an excess of finely levigated iron for 3 hours. This solution contained 65·45 grains of carbonic acid per gallon at the start.

Ferrous Oxide in Solution (by weight)

	Grains per Gallon.
In 1 hour	7·28
" 2 "	1·12
" 3 "	nil

During this time the carbonic acid also fell.

Carbonic Acid in Solution

	Grains per Gallon.
In 1 hour	14·65
" 2 "	10·00
" 3 "	10·00

In 1 hour the sediment was quite black, in 2 hours yellowish brown, and in 3 hours quite brown. Here for the first time in these experiments the metallic iron was in excess; and the iron first taken up into solution soon comes out again and forms a rusty insoluble sediment.

After 3 hours the sediment was filtered off and the clear solution agitated with a small quantity of fresh iron, which it rapidly

converted into a yellowish sediment. As a considerable portion of the carbonic acid had been destroyed and there was no iron in solution, it looked as if this carbonic acid must have been converted into some other acid, and to this extent strengthens the suspicion first created by the extra consumption of permanganate in the previous experiments.

In all the foregoing experiments free oxygen had access to the iron, so that it could not be concluded that the carbonic acid supplied the oxygen. It was therefore decided to take precautions to prevent any access of oxygen in the next experiments.

One litre of recently boiled distilled water was put into an aerator with 20 grammes of levigated iron. The aerator was then screwed up and a cartridge of compressed carbonic acid was liberated into the vessel. The cartridge contained about 8 grammes of carbonic acid, and it was calculated that the internal pressure would be about 60 lb. to the sq. inch. At the end of certain intervals a portion of the liquid was liberated and the amount of ferrous oxide in solution determined.

Ferrous Oxide in Solution

		By Weight.
In 24 hours	25.96
" 48 "	39.41
" 72 "	52.43
" 96 "	65.03

In this case it was quite evident that oxygen was not supplied by the air, as the bottle was under pressure all the time.

The remainder of the solution was allowed to remain in the aerator under pressure, being shaken up occasionally. It was noticed that the liquid, which had at first been clear and colourless, gradually became cloudy and contained ferric hydrate in suspension. A little ferric oxide was also found in solution.

	<i>Ferrous Oxide in Solution.</i>	<i>Ferric Oxide in Solution.</i>
	Grains.	Grains.
In 720 hours	. . 70.0 7.11
" 1000 "	. . 64.1 nil

Here some ferric oxide had been formed and then reduced again. This was probably due to the large excess of levigated iron used.

Another experiment bearing on this point was then made.

The iron was reduced to 10 grammes and used in the form of thin wire, so that it would not expose so large a surface to the liquid. The other particulars remained the same, 8 grammes of carbonic acid, boiled distilled water, and displacement of the air by carbonic acid before adding the water.

		Grains per Gallon.
In 120 hours . .	Ferrous Oxide in solution =	75.60
" " " . .	Ferric Oxide in suspension =	14.98
" 136 " . .	Ferrous Oxide in solution =	78.12
" " " . .	Ferric Oxide in suspension =	18.62

So that not only does carbonic acid oxidize metallic iron into ferrous oxide, but also oxidizes some of the ferrous oxide into ferric oxide, without the intervention of atmospheric oxygen, as in these cases there can be no possible chance of oxygen being supplied by the air.

The residual gas in the aerator after the liquid had been removed consisted of:—

	Per cent.
Hydrogen	50
Carbonic Acid	50

To elucidate the matter still further, another experiment was made in the same way, the only difference being that the amount of iron was reduced to 1 gramme and used in the form of wire.

		Grains per Gallon.
In 24 hours . .	Ferrous Oxide in solution =	5.04
" " " . .	Ferric Oxide in suspension =	nil
" 791 " . .	Ferrous Oxide in solution =	40.32
" " " . .	Ferric Oxide in suspension =	24.36
" 3400 " . .	Ferrous Oxide in solution =	75.60
" " " . .	Ferric Oxide in suspension =	70.00

The bottle was coated with a semitransparent film of hydrated ferric oxide, the amount of this film was not determined, but it should be taken into consideration in estimating the total amount of ferric oxide produced.

Only .065 grammes of the iron wire was left, so that 93½ per cent. had been oxidized and taken into solution.

The following experiment still more clearly illustrates the oxidation of ferrous oxide into ferric oxide by carbonic acid. Into the aerator, prepared as before, equivalent quantities of pure ferrous sulphate and bicarbonate of soda were introduced,

sealed up and the cartridge of carbonic acid liberated into the liquid.

	Ferrous Oxide in Solution, Grains.	Ferric Oxide in Solution, Grains.
At start . . .	252.0 . . .	nil
In 360 hours . . .	214.2 . . .	26.60
" 670 " . . .	116.2 . . .	132.30
" 1200 " . . .	100.8 . . .	145.60

Ratio of Ferric Oxide to Ferrous Oxide

At start . . .	0 : 1
In 360 hours . . .	12 : 1
" 670 " . . .	1.14 : 1
" 1200 " . . .	1.44 : 1

or putting it into diagram form:—

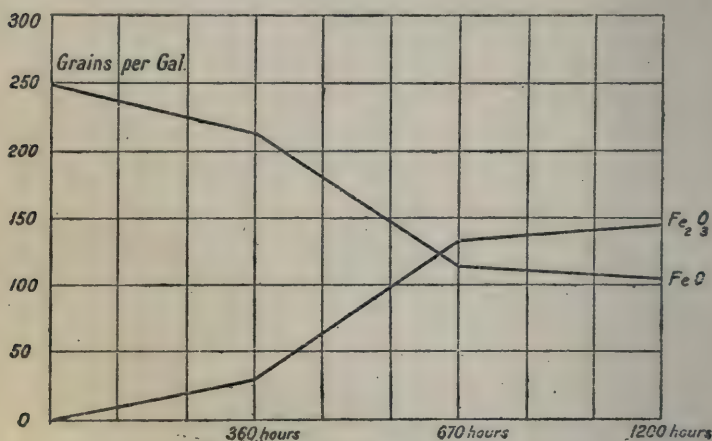


DIAGRAM 20.

The result of this experiment is to show that ferrous bicarbonate is a body in an unstable state of equilibrium, and that after 1200 hours the amount of ferric oxide which was nil at the start, was nearly $1\frac{1}{2}$ times as great as the ferrous oxide.

The solubility and oxidation of iron by carbonic acid alone being no longer in doubt, the question arises: If the carbonic acid parts with its oxygen what becomes of the carbonic acid?

Examination of the Solution

One litre of boiled distilled water was sealed up as before with 10 grammes of iron wire and a cartridge of carbonic acid, all air

having previously been expelled by a stream of carbonic acid gas. In 12 hours there was a considerable quantity of iron in solution, but the liquid was quite clear. In 80-90 hours the solution began to get cloudy, and in 120 hours a brown semi-transparent film of ferric hydrate began to form on the sides of the vessel. The solution was examined at intervals with the following result:—

	<i>Ferrous Oxide by Weight.</i>	<i>Ferrous Oxide by Permanganate.</i>	<i>Ferric Oxide in Suspension.</i>
	Grains.	Grains.	Grains.
In 280 hours . . .	57.96 . . .	62.30 . . .	3.92
" 570 " . . .	71.54 . . .	82.67 . . .	19.04
" 1000 " . . .	69.58 . . .	104.44 . . .	33.60
" 1450 " . . .	34.23 . . .	100.80 . . .	66.64
" 2030 " . . .	24.19 . . .	32.25 . . .	47.60

The differences between the amounts of ferrous oxide found by actual weight and by volumetric determination by permanganate are very marked and show that there is something besides ferrous oxide in the solution, which is destroying permanganate.

The differences are:—

	Grains per Gallon.
In 280 hours	4.34
" 570 "	11.13
" 1000 "	34.86
" 1450 "	66.57
" 2030 "	8.06

Converting these differences into their oxygen value the figures become:—

	Oxygen.
In 280 hours95
" 570 "	2.47
" 1000 "	7.77
" 1450 "	14.78
" 2030 "	1.80

There is here evidence of something besides ferrous oxide, which has an effect upon permanganate, and that the formation of this unknown substance has increased up to 1450 hours.

The amount of iron in solution at 1450 hours has fallen very considerably. At the same time there is apparently no increase in the amount of ferric oxide between 1450 and 2030 hours. This is, however, accounted for by the fact that the inside of the aerator became coated with a film of semitransparent ferric hydrate.

The fall in the ferrous oxide as determined by weight is steady but slight, whilst the permanganate value has come down with

a rush, and there is little more difference in the two values than there was at the 280 hours point.

The accompanying diagram will show these points more clearly.

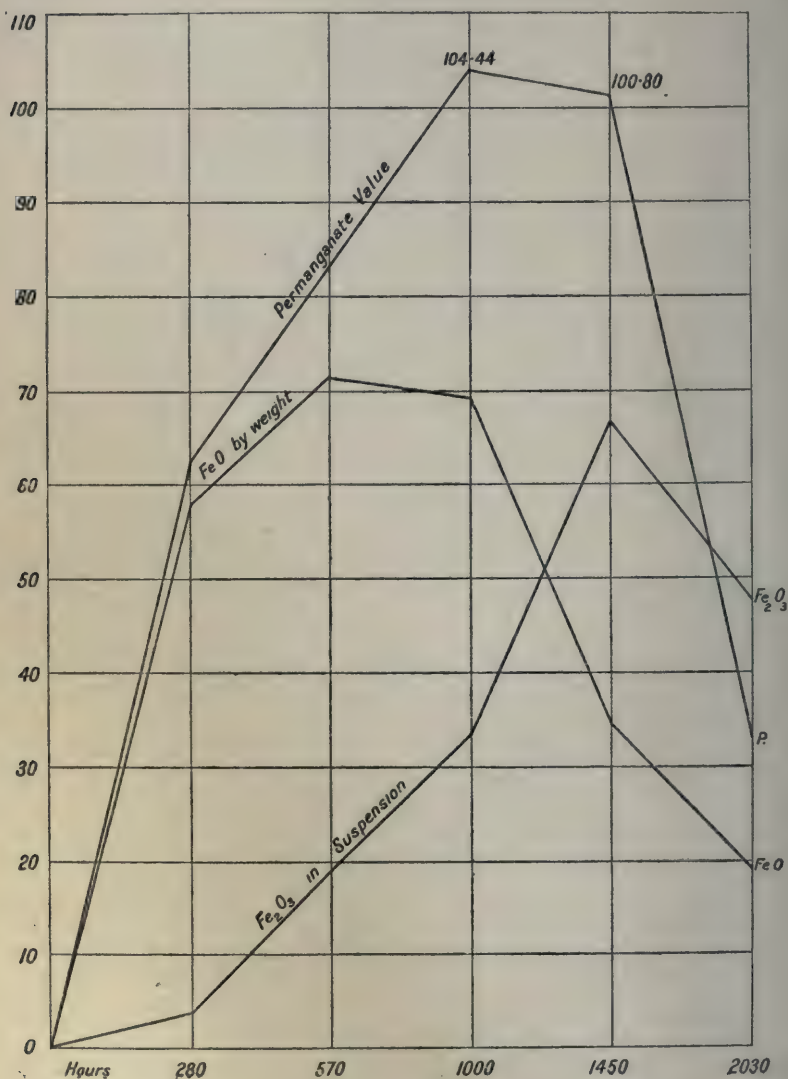


DIAGRAM 21.

The solution of carbonic acid in water was of course acid to start with, but it was found that it soon became alkaline, and a record of these alkalinities taken by Standard Acid with Methyl Orange as indicator, is given in the following diagram.

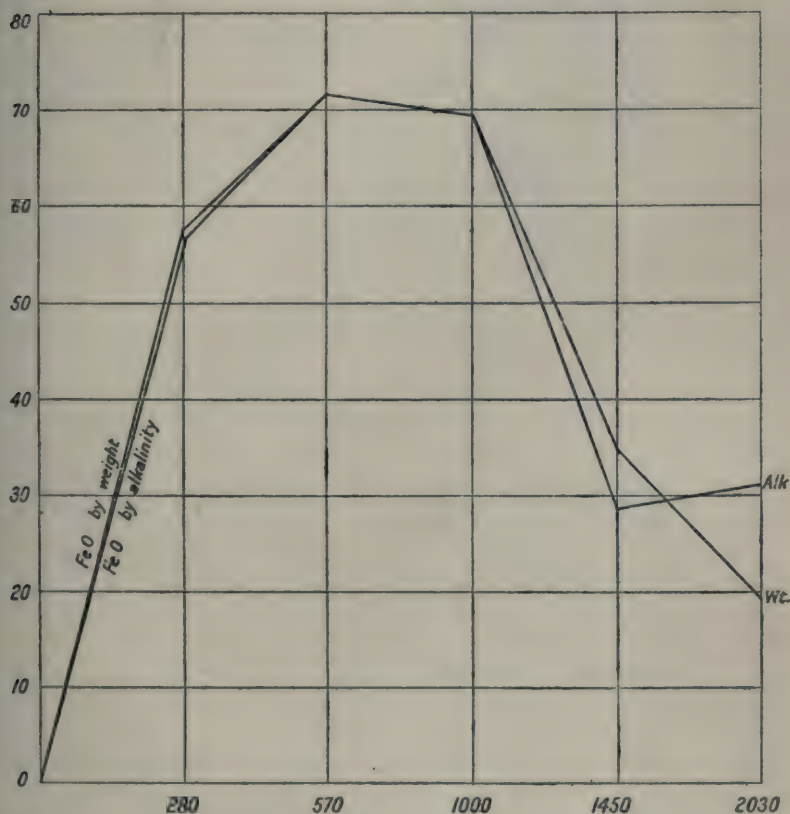


DIAGRAM 22.

This diagram shows that up to 1000 hours the ferrous oxide as determined by weight closely coincides with the value obtained by Standard Acid.

In order to follow the changes more clearly the preceding values have been incorporated into a single diagram.

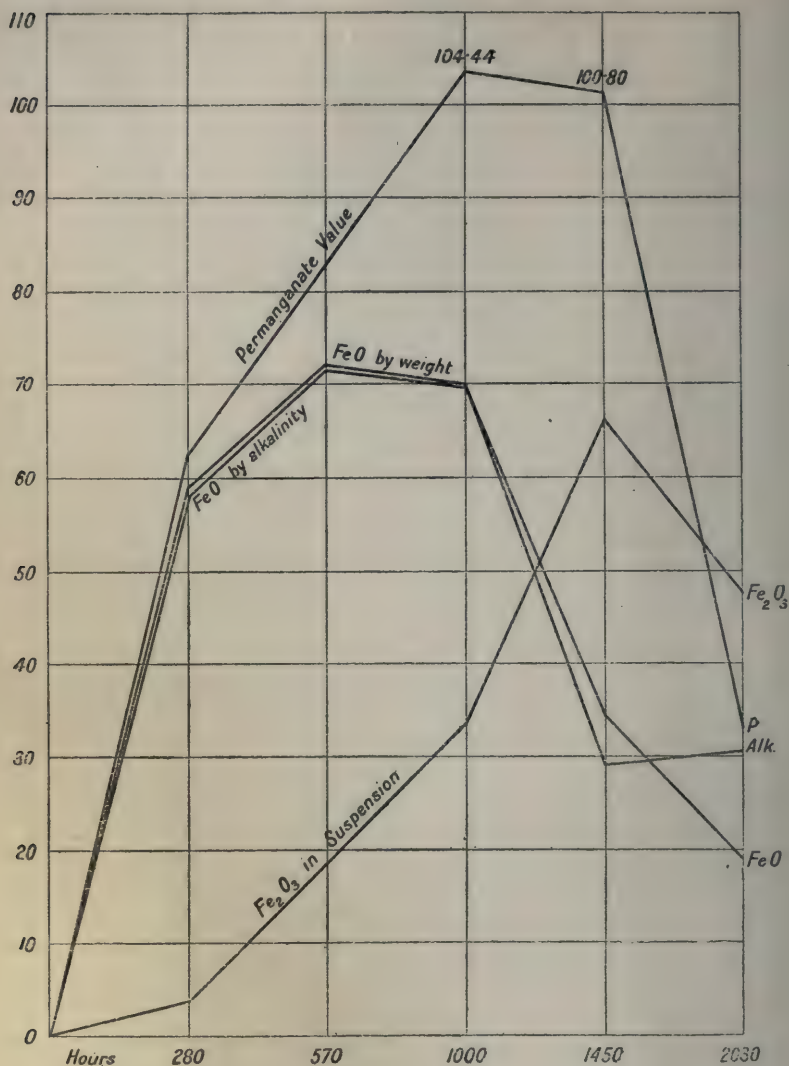


DIAGRAM 23.

A careful inspection of this diagram shows that all the three ferrous values are close together up to 280 hours. In 570 hours the weight and alkalinity values have increased slightly, but are still close together, and the permanganate value has increased much more rapidly. In 1000 hours the alkaline and weight

values, though still close together, have commenced to fall, but the permanganate value has still continued to increase. In 1450 hours the first two values have fallen conspicuously, but are still together. The permanganate value has also commenced to fall, but not nearly in the same proportion. During the next 600 hours, the alkaline and weight values have dropped a little further, but are still in close agreement, the permanganate value has come down with a rush, and all three are again close together.

The ferric oxide up to 1450 hours shows a steady increase. At the end of 2030 hours, although the amount could not be determined owing to adherence to the sides of the vessel, there is no doubt that it had continued to increase and was greater in amount at the end of 2030 hours than it had been at 1450 hours.

These facts tend to show that the high permanganate value is due to something over and above the ferrous oxide formed, and this can only be due to one of the acids formed by the degradation or deoxidation of the carbonic acid present.

Up to the point where the permanganate reaches its highest value, viz. 1000 hours, this acid might be either formic, or glycollic acids, or a mixture of both, as both destroy permanganate. But as this point is the point of maximum reduction reached, it seems probable that the acid formed would be glycollic acid, as any further reduction of this acid must lead to the formation of acetic acid which does not destroy permanganate; hence the sudden drop in the permanganate value from 1450 to 2030 hours.

As these acids are exceedingly difficult to identify in dilute solutions, especially as a powerful reducing agent like ferrous oxide is also present, it was then decided to try the effect of zinc under similar conditions, as zinc oxide does not exert the reducing properties of ferrous oxide. It would therefore be easier to actually identify the acid or acids formed.

The experiment was carried out as before, pure zinc in powder being substituted for the iron wire.

	<i>Zinc Oxide by Weight.</i>		<i>Zinc Oxide by Acid.</i>	
	Grains per Gallon.		Grains per Gallon.	
In 168 hours . . .	41.16	. . .	30.10	
" 306 " . . .	49.00	. . .	39.69	
" 475 " . . .	49.28	. . .	39.69	
" 840 " . . .	40.11	. . .	30.59	

Differences

						Grains per Gallon.
In 168 hours	11.06
" 306 "	9.31
" 478 "	9.59
" 840 "	9.52

At the end of 306 hours, a portion of the contents of the aerator was evaporated to dryness to expel all carbonic acid and render the zinc carbonate insoluble. This residue was washed with boiling water and a soluble zinc salt was dissolved out. The zinc oxide in this salt was equivalent to 8.12 grains per gallon.

Another portion was boiled and evaporated to dryness in the same way, and washed with boiling water. This wash water was then filtered and evaporated to dryness, on gentle ignition it blackened slightly, gave off acid vapours, but eventually burnt quite white.

No permanganate was destroyed by the solution at any of the periods the tests were made.

At the end of 840 hours, the remainder of the solution in the aerator was evaporated to dryness to render the zinc carbonate insoluble. This residue was then treated with boiling water and filtered, and the filtrate distilled with sulphuric acid. The distillate was collected in N/10 Caustic Potash, of which 10.7 c.c. were neutralized. As the distillate destroyed no permanganate, the acid could only be acetic acid, and the quantity calculated from the amount of alkali neutralized works out at 10.5 grains per gallon. The soluble zinc salt was therefore acetate of zinc.

As no permanganate of potash was destroyed by the solution at the periods 168 and 306 hours, up to which time the soluble zinc salt was increasing, it seems highly probable that there has been no intermediate stage in the reduction of the carbonic acid to acetic acid. In this case the reduction seems to be a simple one, and much less complicated than where iron is employed as the reducing agent. In the latter case there is no doubt about the production of formic acid, and there are also some indications that glycollic acid may have been formed at some stage of the process. This experiment with zinc is conclusive evidence that carbonic acid is deprived of some of its oxygen and reduced to one of its degraded forms, while at the same time the zinc is enriched by this oxygen to a corresponding extent. The experiment was designed to show the oxidizing effect of carbonic acid, and in this respect it is highly successful.

The figures are plotted in diagram 24.

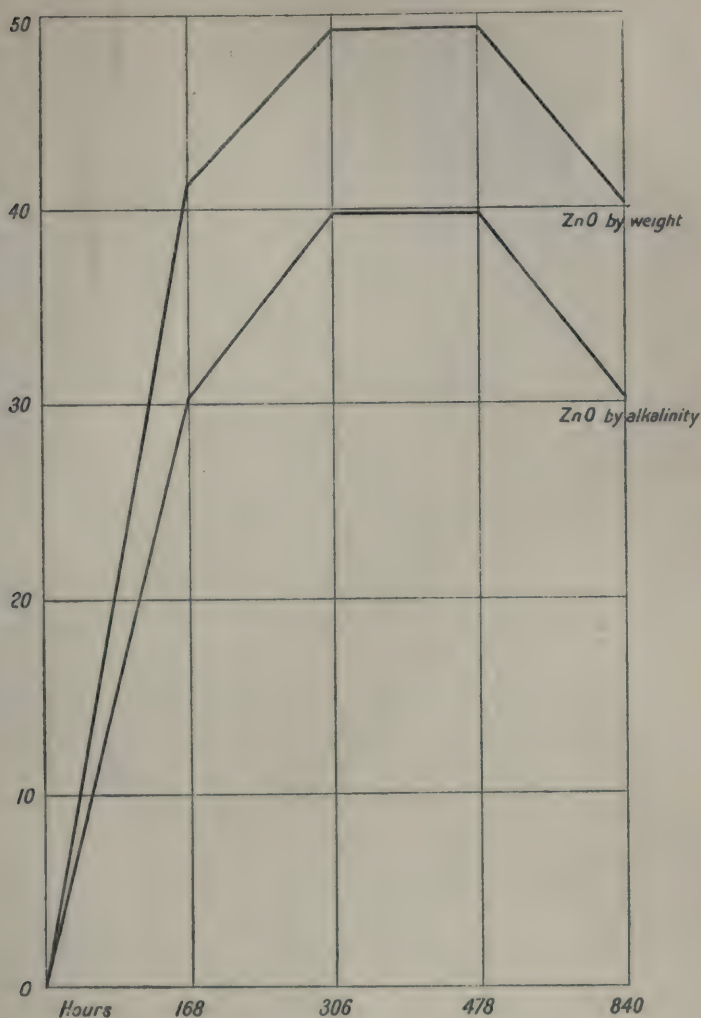


DIAGRAM 24.

After the first week the difference between the zinc acetate and zinc carbonate are almost constant. The drop between 478 and 840 hours seems to point to an insoluble salt being formed, probably a basic acetate; but as the vessel contained an excess of powdered zinc, this deposit could not be distinguished. As zinc is soluble in a solution of carbonic acid,

galvanizing can be little or no protection to iron pipes conveying waters containing free carbonic acid, and can only be effective for a short time.

The following is a diagram of another experiment with iron carried out in the same way for 1100 hours.

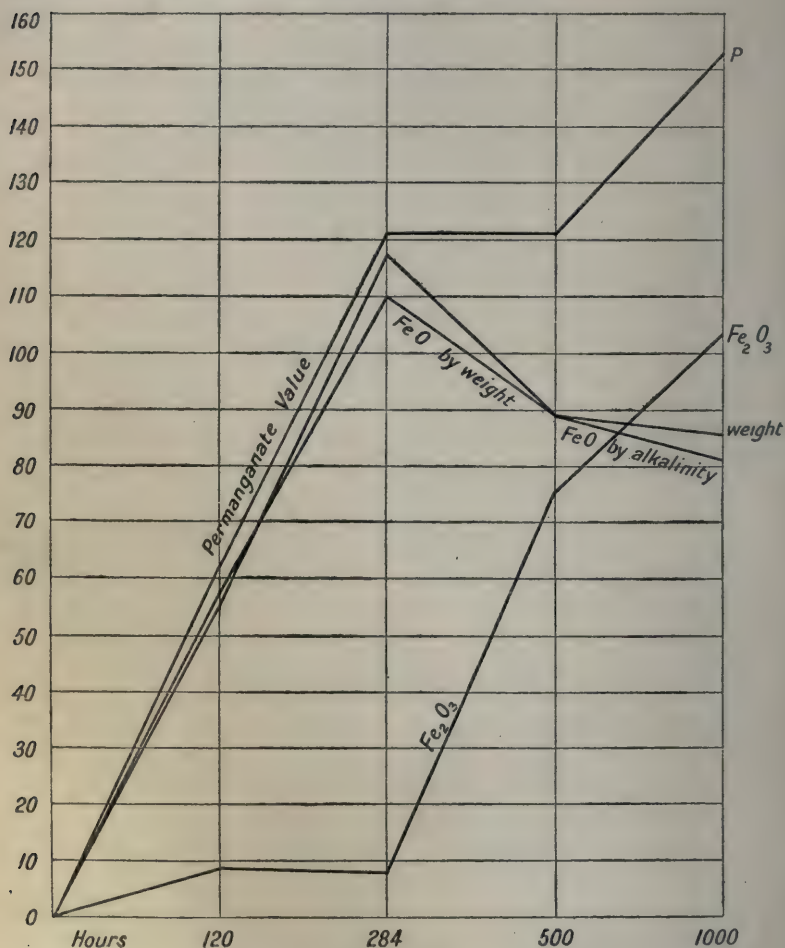
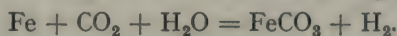


DIAGRAM 25.

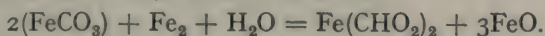
This experiment is a confirmation of the results obtained in the former experiment, and is typical of many others carried out in the same way. In this experiment, although the ferrous

weight value had commenced to drop, neither the permanganate nor the ferric oxide had begun to fall.

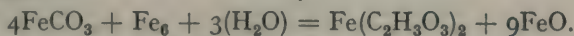
The experiment with zinc conclusively proves that acetic acid is formed by the reduction of carbonic acid, and that at no period during the experiment could any intermediate acid be detected, as no permanganate was decolorized. With iron, on the other hand, intermediate acids are evidently formed as the permanganate value reaches a maximum, and then begins to fall. When this value begins to fall the reduction of the intermediate acid or acids may be considered to have begun. Also in all the diagrams there is a stationary period before the drop takes place, the final result being that all three values approach one another again, and in the end there is not much difference between them. The ferric oxide which started at zero steadily rises all the time, for in all the experiments there was much adhering to the glass. The process of corrosion by carbonic acid in solution, then, seems to be, first some iron is dissolved, ferrous carbonate being formed and some hydrogen set free.



The ferrous carbonate in contact with more iron is converted into Ferrous Formate, and ferrous oxide.

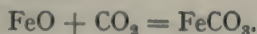


Ferrous glycollate might also be formed according to the following equation:—

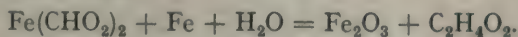


In both cases ferrous oxide is formed to be dissolved up in the excess of carbonic acid still remaining. Although the formation of the glycollate may take place possibly as a transition state between the formate and the acetate, for the sake of simplicity, the formation of formic acid alone will be assumed here.

The ferrous oxide is dissolved by the carbonic acid as long as there is any left to dissolve it:—



When there is no more carbonic acid to reform ferrous carbonate, the ferrous formate is itself decomposed, yielding ferric oxide and acetic acid thus:—



The transformation of metallic iron into ferric oxide takes place without the intervention of any free oxygen, and these experiments go to prove that free oxygen is not an essential in

the process of corrosion. Oxygen alone has very little effect upon iron. Some finely levigated iron was put into a stoppered bottle with boiled distilled water saturated with oxygen. At the end of 6 years no iron could be found in solution and no rust could be observed. Once ferrous oxide is formed oxygen will convert it into ferric oxide, but not so rapidly as carbonic acid. The following experiments illustrate this. Ferrous carbonate was formed by adding bicarbonate of soda to ferrous chloride in equivalent quantities, and the white precipitate so formed was put into a litre of water saturated with carbonic acid. The mixture was agitated by a turbine stirrer for 27 hours, all the time being freely exposed to the air. At the end of that time all the ferrous carbonate had been converted into ferric oxide, and contained no ferrous oxide.

It was calculated from the amount of ferrous chloride put in, that it contained 4.06 grammes of ferric oxide, 4.05 grammes were actually found. The oxide was quite yellow.

In the following experiment caustic soda was used with the ferrous chloride instead of bicarbonate, and no carbonic acid was used. The ferrous hydrate so precipitated was agitated by the turbine as before. In 52 hours it was still black, and at the end of that time it was found to contain 17.28 per cent. of ferrous oxide after washing and drying on the water bath.

The formation of ferric oxide appears to be due to a molecular action rather than to atmospheric oxidation. The conversion of the metallic iron in the aerator takes place in the absence of free oxygen, and where special precautions had been taken to prevent its presence.

This molecular change may be expressed by the equation already given :—



that is, ferric oxide is formed and acetic acid liberated. This formation of acetic acid, which is the lowest acid that can be formed, will account for the drop in the alkalinity curve in diagram 22 and explains why the permanganate value also falls. Acetic acid destroys no permanganate but does destroy the alkalinity value of the ferrous carbonate by converting it into ferrous acetate, a neutral salt. The ferric oxide should go up, but, as already explained, a considerable quantity adhered to the sides of the vessel and was not estimated, and there is no reason to doubt that it really did go up.

That some molecular change such as this does actually take place is confirmed by the following experiments. A neutral solution of ferrous formate was prepared by mixing solutions of pure ferrous sulphate and formate of barium. The latter was kept in slight excess, so that there could be no ferrous sulphate in the solution. The precipitate of barium sulphate was allowed to settle in a stoppered flask, the solution quickly filtered, diluted and boiled. In a very short time first a yellow and then a bright red precipitate was formed. After a time this was filtered off and found to be pure hydrated ferric oxide without a trace of ferrous oxide.

Red Precipitate

Ferric Oxide	91.22
Water of Hydration (diff.)	:	:	:	:	:	:	8.78
							<hr/>
							100.00
							<hr/>

The solution filtered from the red precipitate was slightly acid and still contained a considerable quantity of ferrous salt, but no ferric salt could be detected in solution. The solution was boiled again for many hours, and continued to deposit the same red precipitate.

A slightly acid and stronger solution of ferrous formate was boiled in a flask. In a short time a yellow precipitate made its appearance, but rapidly turned black on further boiling. This was filtered off, washed and rapidly dried. During the drying no yellow tinge could be detected, so it apparently did not absorb oxygen from the air during the process of washing and drying. Analysis showed it to be approximately $2\text{Fe}_2\text{O}_3 \cdot 3\text{FeO}$. The amount of water of hydration was not determined, the examination being confined solely to the ratio of the ferric to the ferrous oxide. This ratio was found to be 112 to 72, which gives approximately $2\text{Fe}_2\text{O}_3 \cdot 3\text{FeO}$ or $\text{Fe}_2\text{O}_3 \cdot 1\frac{1}{2}\text{FeO}$.

The clear solution filtered from the precipitate deposited the red precipitate on further boiling.

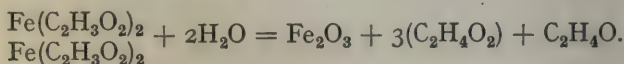
These red precipitates adhere tenaciously to the glass vessels in which they are precipitated and are very difficult to dissolve. Weak acids will not dissolve them, but they are readily soluble in hot concentrated hydrochloric or sulphuric acids. As the solution in acid proceeds the brilliant red colour first disappears, leaving a bright yellow residue, which on further heating suddenly dissolves. In this respect these red precipitates very

closely resemble the red deposits found in boilers where corrosion has taken place.

The deposition of ferric oxide from dilute solution of ferrous formate takes place without the intervention of air, and ferric hydrate is slowly deposited if the solution is kept stoppered up in the cold. In any case the amount of oxygen that could be picked up from the air by a solution boiled in a narrow-necked flask could only be a small fraction of the amount required to form the ferric oxide. The same property is also exhibited by glycollic acid, and ferrous glycollate in dilute solution deposits a hydrate of ferric oxide.

The formation of the ferric oxide would therefore appear to be undoubtedly due to this molecular action, and this molecular action, due to a regrouping of the Carboxyl radicle will explain why carbon does not enter into the composition of these deposits. The molecular action will also explain the red colour of the corrosion deposit inside a boiler, where any free oxygen would be rapidly hurried away into the steam. How far this molecular action is concerned in the production of atmospheric rusting is another question, but as the molecular action invariably takes place in dilute solutions of ferrous formate even if not exposed to oxygen, it is not at all improbable that atmospheric oxygen has been given more credit than it really deserves in the formation of rust.

The formation or deposition of the red precipitate from a dilute solution of a ferrous salt is most immediately and distinctly shown by boiling ferrous acetate. This formation of ferric hydrate necessitates the reduction of the acid, and as acetic acid is the lowest acid of the series, any further reduction must produce an aldehyde. Thus:—

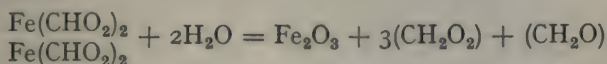


Ferrous acetate is prepared by dissolving iron wire in acetic acid, keeping the iron in excess to prevent the formation of any ferric acetate. This solution is then largely diluted with recently boiled distilled water, and boiled for some hours. A brick red precipitate of ferric hydrate is gradually formed and the solution loses some of its iron, and becomes distinctly acid.

Ferric acetate when boiled does not deposit the red precipitate, which shows that it is the ferrous oxide which reduces the acetate and that the formation of the red precipitate is due to a molecular rearrangement and not to atmospheric oxidation. The red

precipitates are formed whether the solutions are protected from the atmosphere or not.

With ferrous formate the reaction would be expressed by the equation :—



and formaldehyde instead of acetaldehyde would be formed.

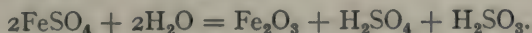
The formation of the red precipitate is more immediate with ferrous acetate than with either glycollate or formate of iron. This should naturally follow, as the acetate is an intermediate step between the formic acid and the aldehyde.

A corresponding result is obtained by boiling a dilute solution of pure ferrous sulphate. In this case a yellow precipitate of pure ferric hydrate is formed, the liquid becomes acid and contains some sulphurous acid.

The precipitate, after being thoroughly washed and air dried, contained :—

Ferric Oxide	83.65
Water (diff.)	16.35
								<hr/>
								100.00
								<hr/>

It contained no ferrous oxide and no sulphuric or sulphurous acid. It was bright yellow in colour and was with difficulty soluble in strong hydrochloric acid. The reaction may be expressed by the following equation :—



The reaction is therefore analogous to that which takes place on boiling dilute solutions of the organic ferrous salts just mentioned.

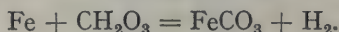
The insolubility of this yellow hydrate in anything but concentrated acids will account for it not redissolving in the dilute acids set free in experiment mentioned.

Corrosion by carbonic acid is due to a molecular rearrangement whereby its oxygen is distributed between the carbon and the iron. Before the corrosion starts the carbon is in possession of all the oxygen, and during the process the iron gradually deprives the carbonic acid of oxygen, destroying its acid properties and forming a deoxidized carbon compound which, having no action upon iron, is free to escape. So long as the carbon is in an acid form it cannot get away, but once the acid properties are destroyed, the residual product is no longer attracted by the iron and escapes from the corrosive cycle.

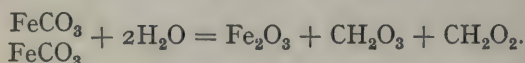
In chemical language the carbonic acid is converted into formic acid and then into aldehyde. The carbon comes into the cycle as CH_2O_3 and leaves it as CH_2O or $\text{C}_2\text{H}_4\text{O}$.

Corrosion is therefore a chemical process, and most probably takes place in the following stages.

(1) The carbonic acid first attacks the iron, forming a solution of ferrous carbonate and setting hydrogen free.



(2) In the presence of water, the ferrous carbonate is broken up into ferric oxide, carbonic acid and formic acid. This reaction can be represented by the following equation:—

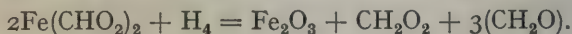


The carbonic acid can either redissolve and again attack more iron, or if there is not sufficient moisture to dissolve it can escape as a gas, but in any case the formic acid, being a liquid and a very much more powerful acid than carbonic acid, is left to make a further attack on the metal.

(3) The action of the formic acid is to dissolve more iron, producing ferrous formate and eliminating more hydrogen.



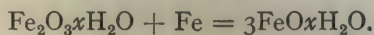
(4) A portion of the ferrous formate so formed is decomposed by the nascent hydrogen, and some formaldehyde is produced.



The formaldehyde is inert and passes out of the cycle so far as corrosion is concerned, while the liberated formic acid is free to start the same series of operations on the iron. At each transformation there is a loss of formic acid owing to the formation of formaldehyde. If the formic acid is not renewed by the influence of more carbonic acid, it will eventually be all converted into formaldehyde, and when this is brought about corrosion will cease.

The principal reaction in all the foregoing cases is the formation of ferric oxide by molecular rearrangement and not by atmospheric oxygen.

Corrosion deposits do contain some ferrous oxide, but the formation of this ferrous oxide may probably be due to a secondary reaction in which metallic iron reduces some ferric oxide.



The ultimate fate of the carbonic acid is conversion into aldehyde. This will account for the entire disappearance of the carbon and will also explain why carbon in some shape or form is never found either in rust or in the corrosion deposits taken from economizer tubes and feed pipes, where the corrosion has been due to free carbonic acid or its degraded compounds.

The reactions just explained probably take place when iron is allowed to rust in moist air, but when carbonic acid corrosion takes place in economizer tubes at temperatures about 140° F. other intermediate reactions no doubt take place.

The carbonic or 246 acid is probably first reduced to formic or 244 acid. This in its turn is reduced to the 243 acid which is glycollic acid, and the 243 acid by further reduction yields the 242 or acetic acid. Any further removal of oxygen means the destruction of the carboxyl group $\text{CO}-\text{HO}$ which forms the acid, so any further reduction to 241 must yield a body which is not an acid. In this case the 241 body is acetaldehyde. When the intermediate acids have been completely converted into aldehyde the corrosion stops and any further change in the character of the deposit is brought about by a secondary reaction, whereby ferric hydrate in contact with metallic iron yields more or less ferrous hydrate.

In the rust cones the formation of the ferrous oxide may also be brought about by the reducing action of the aldehyde. Being confined in the cone and therefore unable to escape, it probably reduces some of the ferric oxide to ferrous oxide, being itself oxidized to acetic acid or other acid. This acid will again attack and dissolve more iron, and this may afford an explanation why the iron is so deeply pitted beneath the cones. The pitting in some cases is so deep that the metal is perforated.

These actions are reversible, and although under certain conditions these acids are reduced to aldehyde with formation of ferric oxide, under other conditions the aldehyde can reduce the ferric oxide and reform the acids. Thus the liquid in the cones, although neutral when sealed up, by reverse action can become acid, and start the same cycle of operations again. It is the oxygen of the carbonic acid and water which oxidizes the iron, and atmospheric oxygen appears to have little or no influence on the reactions, as has been shown in those experiments where ferric oxide was formed by carbonic acid and water alone, without the intervention of any atmospheric oxygen whatever, and where iron in the presence of oxygen without carbonic acid was not corroded at all.

CHAPTER XI

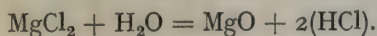
CORROSION

THE corrosion which takes place in boilers is of two kinds: first, the corrosion due to certain salts in the boiler water, and secondly, the corrosion due to slight acidity in the condensed water or to gases in the feed water. In the first case the corrosion usually takes place in the boiler itself, in the second the economizer tubes and feed pipes only are affected.

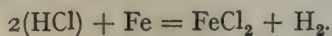
The corrosion of the boiler tubes and water drums is generally caused by one or more of the following salts, which enter into the composition of many feed waters, calcium nitrate, calcium chloride, magnesium chloride and magnesium nitrate.

The corrosion of the economizer tubes is due to carbonic acid or other free acids of a peaty origin, or carboxylic acids derived from the condensed water which is used over and over again as a feed water for the boilers.

Dealing first with magnesium chloride. This salt when present in a feed water is usually in small quantities and is often accompanied by considerable quantities of carbonate of lime, which for a time may prevent its corrosive action. But on evaporation a time comes when all the carbonate of lime has been rendered insoluble and the magnesium chloride has become more concentrated. Heated in contact with metallic iron it undergoes a process of dissociation, whereby it is resolved into magnesium oxide and hydrochloric acid, thus:—

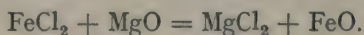


The hydrochloric acid so liberated immediately attacks the iron, dissolving it up as ferrous chloride and liberating hydrogen.

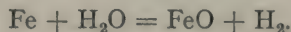


The ferrous chloride so formed is soluble in water and is almost simultaneously attacked by the magnesium oxide which has

been liberated, reforming chloride of magnesium and precipitating insoluble ferrous oxide.



There is no loss of magnesium chloride, which is reformed as fast as it is decomposed, and the reaction may be considered as a reaction in which metallic iron attacks water, the magnesium chloride merely acting as a catalyte, and the net result of the corrosive action may be written in one equation thus :—



It is well known that iron decomposes water or steam at a red heat, but here the catalytic action of the magnesium salt very considerably lowers the temperature at which this reaction takes place. This will also explain why the water is never found to give an acid reaction, and also why iron is not found in solution in the boiler water, or if occasionally so found never to a greater extent than half a grain of ferrous oxide per gallon, which is the limit of solubility of ferrous oxide in water alone.

Thus the quantity of chloride of magnesium never diminishes but always increases as the water is evaporated. If the action were other than catalytic the amount of magnesium chloride would diminish as the corrosion became more aggravated; but the reverse is the case, the greater the corrosion the greater the amount of magnesium chloride, till finally the amount of this salts gets so great that the evolution of acid is so pronounced that part of it is distilled over with the steam before it has had an opportunity of attacking the metal of the boiler.

In this class of corrosion the ferrous oxide formed is black, but as the water coming into the boiler is nearly always fairly well saturated with free oxygen, there is always some free oxygen to act upon the ferrous oxide and convert it into ferric oxide, so that the deposits found in corroding boilers consist of a mixture of the two oxides in variable proportions. As the proportions vary so does the colour of the deposit. The pressure at which the boiler is worked will determine the temperature of the boiler water, which in its turn will determine the state of hydration and more or less modify the colour. At low pressures the deposit is inclined to be yellow, at high pressures dark red.

Sulphate of magnesium, although it does not by itself act so vigorously as magnesium chloride, can become very active, provided chloride of sodium is present, and wherever there is sulphate

of magnesia in presence of chloride of sodium there is potential if not actual chloride of magnesium. Waters which do not contain chloride of magnesium are corrosive provided they contain sulphate of magnesium and chloride of sodium, and as all natural waters do contain chloride of sodium, any water containing magnesia other than as carbonate, may be looked upon with suspicion, for on concentration corrosion will be sure to take place when the water is evaporated on a clean iron surface. If the boiler be already covered with a coating of scale this will prevent the corrosive action, but this action will take place on any clean surface not so covered, and the corrosion so localized may be more destructive than a general corrosion all over the boiler.

The corrosive action of chloride of magnesium can be well illustrated by the following experiment. Finely powdered or levigated iron is put into a stoppered bottle which is then filled up to the brim with a solution of chloride of magnesium. The stopper is then inserted and the bottle allowed to stand for a few days. A disengagement of gas gradually takes place and the bottle is under pressure. After some days if the stopper is released and a light is applied, the hydrogen which has been liberated takes fire and can be seen burning with a pale blue flame. The solution will continue to generate hydrogen, and after every few days the hydrogen can be exploded by applying a light. The iron gradually turns dark green and the volume of the solution gradually diminishes owing partly to the decomposition of the water, and partly to the fact that small quantities are ejected every time the hydrogen is exploded. A convenient strength for the chloride of magnesium solution is about 140 grains per gallon. In order to illustrate the action properly the chloride of magnesium should be quite neutral and should not contain any free acid.

Sulphate of magnesium and chloride of sodium bottled up together with the levigated iron behave in the same way, hydrogen being liberated and the iron converted into a dark green ferrous hydrate.

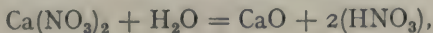
The reaction just described takes place in the cold, and it can readily be understood how very active chloride of magnesium can become when heated. Iron has the property of occluding many times its volume of hydrogen and thereby becoming brittle. This brittleness is another destructive feature in the corrosion caused by magnesium chloride, and is probably the cause of

plates giving way before the actual corrosion has gone very far.

When the magnesium chloride is accompanied by carbonate of lime, the magnesium chloride is decomposed by the carbonate of lime, forming calcium chloride, and the magnesia which is set free remains free and floats about in the boiler water. It is for this reason that chloride of calcium is always found in boiler waters into which sea-water finds its way, and also that magnesia is found floating about the boiler water or imprisoned in the crystalline scale. Although chloride of calcium has not such a powerful catalytic action as the chloride of magnesium, it nevertheless does act as a corrosive agent. On the other hand, sulphate of lime, being insoluble in high-pressure boiler water, is not a potential source of chloride of calcium. It is rather the other way about; if the water contained chloride of calcium and sulphate of sodium, sulphate of lime, being insoluble, would be formed and chloride of sodium remain in solution.

Nitrate of lime and nitrate of magnesia also act as powerful corrosive agents when they are allowed to concentrate in boiler waters. In these cases the corrosion can either be explained as a catalytic action or explained by a series of chemical equations, the reactions described by the equations taking place simultaneously, so that the water is never found to be acid.

With nitrate of lime these reactions would be



that is, the nitrate of lime in contact with metallic iron is resolved into free lime and nitric acid. The nitric acid then immediately acts upon the iron to form nitrate of iron and give off hydrogen.



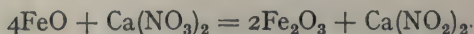
The lime which has previously been set free now acts upon the nitrate of iron, precipitating ferrous oxide and reforming nitrate of lime.



In this case the ultimate result of the reaction should be the formation of ferrous oxide and the elimination of hydrogen, the nitrate of lime suffering no diminution; this, however, is not actually the case, for the liberated hydrogen removes oxygen from the nitrate and reduces some of it to nitrite of lime.

At high pressures there is a further reaction by which the

ferrous oxide is oxidized to ferric oxide, the nitrate of lime at the same time losing an equivalent of oxygen and becoming converted into nitrite of lime.



That this action does take place is illustrated by the following experiment which was carried out in order to prove this point.

Finely divided iron was agitated for several hours with solution of nitrate of lime. The iron was seen to rust very rapidly and soon turned quite yellow.

The solution of the nitrate, which was quite neutral, contained .82 per cent. of nitrate of lime before the experiment was started and contained no nitrite, but at the end of the experiment the solution was found to contain .0104 per cent. of nitrite of lime and to be slightly alkaline, so that $12\frac{1}{2}$ per cent. of the nitrate had been converted into nitrite.

The corroded iron, which was quite yellow, contained no ferrous oxide, and after being air-dried contained:—

Ferric Oxide	76.54
Water of Hydration	23.46
	<hr/>
	100.00
	<hr/>

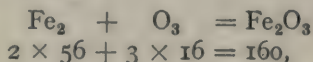
Here the oxidation of the iron is complete, and this oxidation has taken place at the expense of the oxygen of the nitrate. No doubt if the experiment had been stopped at an earlier stage some ferrous oxide might have been found, but the object of the experiment was to prove the corrosive effect of the nitrate of lime. It is well known that ferrous oxide is converted into ferric oxide by nitrates, but it is not so well known that nitrate of lime attacks iron.

The strength of the nitrate of lime solution may appear very weak when looked at from the percentage point of view, but it is really a fairly strong solution when translated into grains per gallon and looked at from a boiler-water point of view. A solution containing .82 per cent. nitrate means a solution containing 574 grains per gallon, an amount frequently reached in boiler waters.

This experiment was carried out in the cold, and as it is a well-established fact that the action is much accelerated by heat, it will be seen how destructive an agent nitrate of lime can become.

An engineer no doubt would be more satisfied if the amount of iron had been weighed before and after the experiment, and the amount of corrosion actually measured and weighed, but as this is a chemical reaction this is not necessary, and the amount of oxidation can readily be calculated from the loss of oxygen in the solution.

The volume of solution was 1 litre, and it was made by using recently boiled distilled water and kept well covered up during the experiment to prevent any atmospheric oxidation. The amount of nitrite of lime in the whole volume of solution was therefore .104 grammes, and as 132 parts of nitrite of lime mean 32 parts of oxygen given up, .104 grammes would mean approximately .26 grammes oxygen.



and as 112 parts of iron require 48 parts oxygen, the amount of iron oxidized in the experiment was approximately .6 grammes, and the amount of ferric oxide formed .83 grammes.

Waters containing nitrate of lime and which are neutral in the cold or as fed into the boiler, on concentration become slightly alkaline and the boiler water gives a pink colour to phenolphthalein. This pink colour, which is due to a little lime set free, is often misleading, as it is assumed that the water has a soda alkalinity sufficient to prevent corrosion, whereas as a matter of fact, the slight lime alkalinity is not sufficient to prevent corrosion, and for this reason boilers may be undergoing active corrosion, although all the time the boiler water has shown a red colour to phenolphthalein. Nitrate of lime is a frequent constituent of feed waters and is always broken up in the way described if steps are not taken to destroy it before it enters the boilers. Unless a full analysis of such a water is made the nitrate of lime may be overlooked, especially if the analysis only gives the temporary and permanent and records the alkalinity in terms of carbonate of lime. In this case the nitrate of lime would be concealed under the permanent hardness. Permanent hardness may mean anything that destroys soap and is not removed by boiling the water for half an hour; thus all lime and magnesia salts except the carbonates would come under this designation. As the salts constituting the permanent hardness of a water are the salts which cause corrosion, more attention should be given to the permanent than to the temporary hardness. The latter

can at worst only produce an inconvenient scale, whereas the former can cause disastrous corrosion, and where explosion has taken place owing to a thinning of the plates, the wasting has in most, if not in all cases, been brought about by the permanent hardness. Of course the wasting may be brought about by the intrusion of acid into the boilers, but as acid is a soap-destroying body, this would be measured as part of the permanent hardness, if only the soap tests were used in the examination of a water.

As the soap test is merely a record of the soap-destroying power of a water, too much reliance should not be placed on the results. The results are only approximate and at best convey very little useful information. The only advantage the soap test possesses is the ease and rapidity with which the test may be made. Where a full analysis of the water has already been made and the character well known, the soap test may be useful as a rapid means of determining any variation, but beyond this it does not furnish much real information. At best it is only a record of how much of a particular solution of soap is destroyed by the water. The standard solution of soap cannot be made by weighing out a certain definite quantity of soap and dissolving it up in weak alcohol, but has to be made by actual trial; that is, the solution has to be made to correspond to a standard solution of a lime salt (generally chloride of calcium) by trial and error, by adding more soap or diluting the original solution until the desired result is obtained. By this means a standard solution of soap is obtained which is made to correspond with a solution of calcium chloride of a certain strength. It is only accurate for that strength, and it is accurate for that strength alone, as any one conversant with testing waters by the soap method is painfully aware. In addition to its limited accuracy it does not discriminate between the various salts constituting the permanent hardness.

If it be desired to know the hardness of a water, this can be calculated from the analysis and recorded as carbonate of lime. If the carbonate hardness be deducted from the total hardness, the result will be the permanent hardness. The hardness calculated in this way gives a better idea of the water than the hardness obtained by the soap test. The soap test records the temporary hardness as the loss of hardness on boiling the water at ordinary atmospheric pressure for half an hour, whereas the carbonate hardness will give the amount of carbonates (calculated

as carbonate of lime) which will be deposited when the water is heated under pressure in the boilers.

Nitrate of magnesia behaves like nitrate of lime as a corrosive agent, but owing to the insolubility of magnesia, the water only gives a very faint pink colour to phenolphthalein; for this reason magnesium nitrate is not so liable to give a false idea of alkalinity as nitrate of lime, although it is at the same time reduced to nitrite of magnesia; indeed, all the nitrates, even nitrate of sodium, are partly converted into nitrites in boilers working at high pressure, and it is the exception rather than the rule not to find some nitrites in boiler waters where the original water has contained a nitrate.

Some soft natural waters are slightly acid and cause pitting in the boilers and also form red or black deposits. The following are cases:—

Feed Water

Sulphate of Lime53
Sulphate of Magnesia27
Chloride of Sodium40
Hydrochloric Acid41
Organic Matter38
		<hr/>
		1.99
		<hr/>

Deposit in Boilers

Silica73
Ferrous Oxide	25.60
Ferric Oxide	65.58
Water of Hydration, etc.	8.09
		<hr/>
		100.00
		<hr/>

Boiler Water

Ferrous Chloride	1.50
Sulphate of Lime	8.01
Sulphate of Magnesia	7.46
Sulphate of Sodium	3.32
Chloride of Sodium	10.09
Hydrochloric Acid	1.63
Organic Matter	8.17
		<hr/>
		40.18
		<hr/>

A little caustic soda put into this water to neutralize the acid would have prevented the corrosion.

BOILER CHEMISTRY

Feed Water

Silica	·10
Oxide of Iron	·12
Formate of Lime	1·04
Sulphate of Magnesia	·66
Chloride of Sodium	·80
Formic Acid	·64
	<hr/>
	3·36
	<hr/>

Boiler Water

Silica	·20
Ferrous Chloride	1·79
Sulphate of Lime	16·86
Sulphate of Magnesia	10·20
Chloride of Magnesia	23·37
Chloride of Sodium	182·60
Hydrochloric Acid	·51
	<hr/>
	235·53
	<hr/>

Deposit in Boilers

Silica	9·80
Ferrous Oxide	10·08
Ferric Oxide	26·16
Sulphate of Lime	40·22
Magnesia	7·42
Organic Matter	1·40
Water of Hydration, etc.	4·92
	<hr/>
	100·00
	<hr/>

Deposit in Tubes

Silica	1·38
Ferrous Oxide	11·81
Ferric Oxide	76·22
Water of Hydration	6·52
Organic Matter	4·07
	<hr/>
	100·00
	<hr/>

In this case the boiler was completely ruined through general corrosion, the wasting was general and the metal was gradually eaten away.

Such cases as these are somewhat unusual, but in soft-water districts they do exist and give much trouble if not properly dealt with. These waters are usually little if anything more than rain-waters, and derive their acid either from the air of manufacturing districts or from peaty matters in the districts where they are collected. Occasionally the acid may be derived from the

pollution of rivers. Usually an acid water is a soft water, as it has been collected from basins composed of nothing but insoluble siliceous material.

The following is a case in which a carbonate of lime water can be made to cause corrosion. The original water was a London water of 14.0° Hardness, the full mineral analysis of which is as follows:—

Town Water

Silica	·17
Oxide of Iron	·10
Sulphate of Lime	1·36
Carbonate of Lime	10·60
Nitrate of Lime	1·44
Sulphate of Magnesia	1·74
Chloride of Sodium	3·28
	<hr/>
	18·69
	<hr/>

As the water in this condition was too hard for boiler feed it was decided to soften it down to about 4°, but the softening was not to go below this. The consequence was that the boilers soon showed signs of corrosion, and the matter had to be investigated. An analysis of the softened water showed it to contain:—

Softened Water

Silica	·10
Oxide of Iron	·07
Sulphate of Lime	1·36
Carbonate of Lime	·74
Nitrate of Lime	1·44
Sulphate of Magnesia	1·20
Sulphate of Sodium	·58
Bicarbonate of Sodium	2·34
Chloride of Sodium	3·28
	<hr/>
	11·11
	<hr/>
Hardness	4·00°

The result of the softening had been to remove practically the whole of the carbonate hardness, leaving a small quantity of bicarbonate of soda to give it an alkalinity. On boiling this water the bicarbonate is of course converted into carbonate of soda, the amount of which is not nearly sufficient to destroy the sulphate of lime, nitrate of lime and sulphate of magnesia; the consequence being that nitrate of lime and sulphate of magnesia

accumulated in the boiler water and caused active corrosion. In this case the decision not to soften below 4° was the cause of the trouble. Had the water been properly softened the whole of the permanent hardness would have been destroyed and no nitrate of lime left in the water to cause corrosion. It would have been better not to have softened the water at all, as then the carbonate of lime scale would have acted as some sort of protection, but the entire removal of the carbonate of lime prevented this scale being formed.

There are many hard waters of a similar character, which will become causes of corrosion, if the carbonates only are removed in the process of treatment. This is not infrequently done on the plea that a water for boiler feed must not be too soft, as a soft water causes corrosion. This is a fallacy. It is not because the water is soft that corrosion is set up, but because the soft water contains a small quantity of some corrosive substances, and the practice of only removing the carbonates and leaving the corrosive materials such as nitrate of lime and chloride of magnesium to remain in the water without the inhibitory action of these carbonates is, to say the least, irrational, and founded on a false assumption.

The following is an example of a natural water without any carbonate of lime at all, the small amount of carbonate it contained being in the form of ferrous carbonate. On exposure to the air the ferrous carbonate is deposited as ferric hydrate.

<i>Water</i>	
Silica	14
Ferrous Carbonate	1.62
Sulphate of Lime	1.90
Chloride of Calcium	5.13
Chloride of Magnesia	3.24
Chloride of Sodium	13.53
	<u>25.56</u>
Hardness	11.00°

The boiler water produced by evaporating this water caused considerable corrosion, as was to be expected from the character of the water. An analysis of this boiler water is given on next page, as it is a good example of what happens in a boiler. A glance at the analysis will be sufficient to show its corrosive character.

Boiler Water

Sulphate of Lime	15.38
Chloride of Calcium	227.67
Chloride of Magnesia	120.82
Chloride of Sodium	754.40
	<hr/>
	1118.27
	<hr/>

The following is a case of corrosion and scale at the same time. The boiler was covered in most places with a hard white scale, but in places showed red patches where it was evident that bleeding was taking place and active corrosion going on.

On analysis the white or pinkish scale was found to consist principally of sulphate of lime, with about 12 per cent. of the oxide of iron. Its full composition was:—

Pink Scale

Silica44
Ferrous Oxide	2.88
Ferric Oxide	8.80
Sulphate of Lime	80.43
Magnesia	6.56
	<hr/>
	99.11
	<hr/>

Red Deposit on Unprotected Parts

Silica42
Ferrous Oxide	29.10
Ferric Oxide	64.00
Sulphate of Lime	5.80
Magnesia77
	<hr/>
	100.09
	<hr/>

The composition of this red deposit showed that active corrosion was going on, and the entire absence of carbonate of lime in either of the deposits pointed to a boiler water which was not alkaline. This was borne out by an analysis of the boiler water. This analysis showed that the boiler water was actively corrosive and scale-forming at the same time, and confirmed the conclusion drawn from the deposits.

Boiler Water

Sulphate of Lime	15.69
Nitrate of Lime	21.52
Chloride of Calcium	54.47
Chloride of Magnesia	3.15
Chloride of Sodium	580.00
	<hr/>
	674.83
	<hr/>

Another example of a corrosive boiler water is given below.

Corrosive Boiler Water

Silica	20
Oxide of Iron	10
Calcium Hydrate	41
Sulphate of Lime	8.74
Chloride of Calcium	214.30
Nitrate of Lime	11.48
Chloride of Magnesia	6.29
Chloride of Sodium	577.30
	<hr/>
	818.82
	<hr/>

That this water is highly corrosive will be seen from the analysis of the scale taken out of the boiler containing this water.

Scale

Silica	5.86
Ferrous Oxide	19.58
Ferric Oxide	54.00
Sulphate of Lime	3.77
Carbonate of Lime	2.38
Magnesia	7.11
Water of Hydration, etc..	7.30
	<hr/>
	100.00
	<hr/>

This scale contains 75.76 per cent. of iron calculated as ferric oxide, so that very extensive corrosion had been going on. The boiler water had only a faint lime alkalinity which was not sufficient to protect the boiler from the corrosive action of the chloride of calcium, nitrate of lime and chloride of magnesium. This faint lime alkalinity probably led to the conclusion that the boiler water was in good condition, as it gave a pink colour to phenolphthalein. Had the quantity been measured by Standard Acid it would at once have been seen that this alkalinity was not nearly sufficient to preserve the boilers from corrosion and to prevent the formation of a scale containing 76 per cent. oxide of iron.

CHAPTER XII

CONDENSED WATERS

By condensing the exhaust steam and using it over and over again as a boiler feed, is a way out of the incrustation difficulty so far as the boiler itself is concerned, but there is always a certain loss of steam which has to be replaced by a make-up of Town or other available water. The methods of condensing are now so good that in a well-designed and properly worked plant the make-up is reduced to about 5 per cent. This will immediately reduce the trouble from scale and concentration to a corresponding extent, and if at the same time the make-up is softened these troubles can be very much further reduced. This, however, introduces another complication, viz. corrosion in the economizers. The condensed steam is nearly always slightly acid, and the make-up water generally saturated with free oxygen, and also often contains free carbonic acid. These acids, either in the presence of free oxygen, or even in its absence, have a very corrosive action upon iron, either as mild steel or in the form of cast iron, and economizers become corroded and in some cases badly pitted by the action of the condensed feed waters.

Corrosion in the economizers shows itself in two ways: first, by the formation of a red deposit, and secondly, by the formation of rust cones and pitting of the metal. As in many cases in which the corrosion occurs, the feed water is little more than distilled water and seldom contains even 1 grain of mineral matters per gallon, the cause of the corrosion must be looked for in the non-mineral matters in the water. The gases are oxygen, carbon dioxide and nitrogen. The latter may be at once dismissed as it is an inert gas which has no action on either iron or water. Oxygen alone, even in the presence of water, has very little if any action on iron, but, as has already been shown, carbonic acid has a very decided corrosive action upon iron.

The usual cause of the corrosion is carbonic acid itself or some other carboxylic acid derived from and so closely related to

carbonic acid that it is difficult to distinguish between them when they exist in such a dilute state.

The steel or mild iron used in modern boilers is, physically speaking, a much more perfect material than iron formerly used in boilers working at lower pressures. Not only is it designed and manufactured to stand higher pressures, but in withstanding this higher pressure it is subjected to chemical reactions in the boilers which did not take place at the lower pressures formerly employed. The metal is therefore often exposed to a new set of conditions, and as boiler practice has now reached a stage in which the boilers can be fairly well protected from incrustation, the metal no longer covered up by a protective covering of scale is subjected to the influences of what is often little more than distilled water. The steel itself is an alloy containing minute quantities of carbon, manganese, copper, silicon, sulphur, phosphorus, etc., in the form of alloys. These alloys are not equally resistant to the action of the corroding influence, and possibly set up galvanic action that increases the corrosion in places and prevents it in others. Some parts are eaten away and others remain intact, the consequence being a very unequal form of corrosion, and the metal appears as if it had been perforated in places. This pitting action is often produced by what are called rust cones. The rust cones are usually associated with the corrosion which for want of a better name is called carbonic acid corrosion. It is by no means certain that it is the carbonic acid which is the actual corroding agent, although it may be the primary cause of the corrosion. As has been shown in the experiments with carbonic acid and iron, the carbonic acid is first of all reduced to formic acid, and it is probable that the free carbonic acid in condensed steam is in reality formic acid. In either case the formic acid, once formed, dissolves up a certain quantity of iron, and by molecular action this solution of ferrous formate is broken up into ferric hydrate and other organic bodies.

This deposit of ferric hydrate is exceedingly tenacious and obstinately adheres to the surface on which it is formed. The deposit in places is gradually built up into a cone and some liquid is finally imprisoned within its walls. Some of the corrosive water is thus confined and protected from the flow or current of the water, and its influence is thus confined to one particular spot. Being protected by the walls of the cone the imprisoned liquid is compelled to limit its action to that particular spot, hence inside the cone the iron is deeply pitted. On breaking

these cones the pit marks are plainly visible and the inside walls of the cone are black, not yellow or red. Where the deposit has not adhered and is loose, the dilution and boiling in the water converts it into the red hydrate so characteristic of boiler corrosion. There are therefore three distinct forms in which the oxide of iron occurs in a corroding economizer: (1) the yellow hydrate forming the outer walls of the cones, (2) black ferrous hydrate inside the cones, and which turns yellow on exposure to the air, and (3) the red hydrate found loose in the channels where the current is least.

The rust cones have a composition such as the following. This specimen was taken from an economizer where the corrosion was due to carbonic acid.

Rust Cones

Silica	1.20
Ferrous Oxide	25.92
Ferric Oxide	70.16
Water of Hydration, etc.	2.72
	<hr/> 100.00 <hr/>

The red deposit found loose in the same economizer contained:—

Red Deposit

Silica	1.42
Ferrous Oxide	7.49
Ferric Oxide	85.76
Oil	1.94
Water of Hydration	3.39
	<hr/> 100.00 <hr/>

The composition of the rust cones differs from that of the red deposit mainly in the greater percentage of ferrous oxide.

The accompanying analyses show the composition of other specimens of the red deposit found in economizers. They are all taken from boilers in which the corrosive agent was originally carbonic acid. The analyses show that they vary little in composition, and that the ferrous oxide is small compared to the ferric oxide.

Economizer Deposits

Silica26
Ferrous Oxide	8.64
Ferric Oxide	89.12
Water of Hydration	1.98
	<hr/> 100.00 <hr/>

BOILER CHEMISTRY

Silica	40
Ferrous Oxide	7.20
Ferric Oxide	84.50
Oil	3.50
Water of Hydration	4.40

100.00

Silica	22
Ferrous Oxide	9.22
Ferric Oxide	79.24
Oil	4.20
Water of Hydration, etc.	7.12

100.00

Zinc is also attacked by carbonic acid, and the following analyses from galvanized tubes illustrate how the zinc is gradually removed and the iron laid bare.

The principal constituent in the deposit is first of all oxide of zinc, with a small quantity of the oxide of iron, but as the zinc is removed the oxides of iron become the dominant constituent.

Economizer Deposit

Silica	24
Ferrous Oxide	6.88
Ferric Oxide	34.60
Oxide of Zinc	58.00

99.72
Economizer Deposit (eight months after)

Silica	64
Ferrous Oxide	22.60
Ferric Oxide	71.06
Oxide of Zinc	5.80

100.10

Both these deposits were dried at 212° F. before analysis. When taken out of the boiler probably both contained some water of hydration.

Another specimen from a galvanized tube, when most of the zinc had gone had the following composition :—

Economizer Deposit

Silica	34
Ferrous Oxide	10.08
Ferric Oxide	79.36
Oxide of Zinc	6.64
Water of Hydration	2.76
	<hr/>
	99.18
	<hr/>

Although the explanation here given shows how pitting takes place, it does not afford any actual reason why one spot more than another should be attacked and should be subject to the formation of the rust cones. This is most probably determined by the position of some one or more of the alloys which are less resistant to the corrosion than the other alloys, and the reason will have to be looked for in the metallurgical structure of the metal. There can be little doubt that phosphide of iron, or the alloy of manganese and iron, is less resistant to the action of carbonic acid than carbide or silicide of iron, and the rust cones once formed, the most active corrosion is confined to these spots.

The accompanying illustration is taken from a photograph of a corroded economizer tube. The cones had been scraped off, and the tube cut and straightened out.

Corrosion, once started, is difficult to arrest, as the corrosive action continues for a long time after the active corrosive agent has been removed, and it requires some alkali in the water to exert an inhibitory action and prevent the extension of the corrosion once started.

This alkali can be either free lime, in the form of calcium hydrate, or caustic soda; each has its advantages and disadvantages. Lime will come out of solution when the amount in the boiler water reaches 5 or 6 grains per gallon, that is, about 10° Hardness. Any amount over and above this will come out of solution either as a sludge or as a scale. The lime scale, except in considerable thickness or cemented together by a sulphate scale, is not a bad scale. When, however, it is accompanied by much sulphate of lime it does form a rather bad scale. If the water at the same time contains any considerable quantity of silica, then a silicate of lime scale will be formed which is very destructive to the tubes. Caustic soda, on the other hand, can accumulate in the boiler water to almost any extent without coming out of solution. The amount can easily be regulated by the blow-off cock, and can in this way be kept down to any desired

degree of concentration. Here, again, silica can form a very bad scale, if any lime or magnesia salts are left in the make-up water. The silica is first dissolved in the caustic soda with the formation of silicate of soda. This silicate of soda reacts upon the lime or magnesia salt in solution forming silicate of lime or magnesia, both of which form a hard, tenacious, non-porous scale which soon causes blistering of the tubes. Whether it is better to use lime or soda as the inhibitory alkali will therefore depend largely upon the character of the make-up water and the working conditions of the boiler. It is not enough to merely neutralize the water, there must be a slight excess of the alkali to exert an inhibitory action, and the quantity of alkali so required varies with the character of the water. In some cases the excess may be very small, in other cases considerably larger. In many cases it is advisable to have both lime and caustic soda, especially if the make-up water contains organic salts. The lime often removes these in an insoluble form in which they are not so liable to be broken up by the heat of the boiler as the corresponding soda salts. The soda salts are broken up at the boiler temperature and yield products which contaminate the steam and thus render the condensate again corrosive. Lime, on the other hand, prevents this contamination, and it is advisable to use lime where the quantity required and the boiler conditions will permit. But before deciding upon the character and quantity of alkali to be used it is essential that the characteristics of the water to be used as a feed should be as accurately known as possible. Even then it is often a question of trial and error before the better alkali and the correct quantity is determined, and much damage can be done by an indiscriminate use of lime or caustic soda.

To prevent the corrosion, any acidity in the condensed water must be neutralized and free carbonic acid must be prevented from getting into the system. Fortunately it is a comparatively easy matter to deal with this free carbonic acid. The removal is best effected by calcium hydrate, and this can easily be introduced into the mixture of soda ash and calcium hydrate used for treating the make-up. As calcium hydrate is a material of constant strength and quickly soluble, any required excess can immediately be given to the make-up. In this way the make-up can be rehardened with sufficient excess of calcium hydrate to deal with the free acid in 10, 20, or 30 times its own volume of condensed water. When the whole of the free acid has been



CORRODED BOILER PLATE

NOTE. In certain lights the crater holes appear as protuberances, but by varying the angle of light or by using a magnifying glass, the pit-holes appear in their true aspect.

eliminated from the system, the amount of calcium hydrate to be used can be very materially reduced. The excess used in treating the water will always ensure the complete elimination of free acid from the make-up, no free acid can therefore go forward and the corrosion will be arrested. It is, however, always advisable to leave a very slight quantity of calcium hydrate in the feed water so as to protect the economizers; this quantity can be in some cases reduced to .2 grains per gallon, and it will be a long time before this quantity can give any appreciable scale in the boilers. This lime alkalinity will never accumulate to any extent in the boiler water, as it is only very slightly soluble in water at the temperature and pressure reached in the boilers. It will come down partly as a sludge and partly as an egg-shell scale in the tubes, but it will require a long time before it causes any trouble, and precautions can be taken to keep down the excess to proper limits. On the other hand, if a considerable excess is used a lime scale such as the following will be produced.

Lime Scale

Silicate of Lime27
Oxide of Iron80
Calcium Hydrate	94.35
Sulphate of Lime	2.65
Carbonate of Lime	1.75
Moisture, etc.18
	<hr/>
	100.00
	<hr/>

This is a comparatively soft scale and easily removed by the turbine cleaners, but there is no necessity for it to be formed at all if proper precautions be taken to keep down the quantity of excess calcium hydrate. It is a question of adjustment of quantities, and the principle of the method is to use just sufficient calcium hydrate to arrest the corrosion without at the same time forming a lime scale.

In treating the make-up for mixing with the condensate it is always advisable to use a slight excess of soda ash. First of all there is a certain quantity of soda ash required to destroy the permanent hardness of the water. If this be sulphate of lime it will form a very hard scale, and if it be nitrate of lime or magnesia it will cause corrosion, but if a slight excess of soda ash be used these will be destroyed, and the excess of soda ash in presence of the excess of calcium hydrate will be converted into caustic soda, which will go forward into the boilers and keep

the boiler water sufficiently alkaline to prevent corrosion. Calcium hydrate alone is not a sufficiently strong alkali to protect the boiler tubes from corrosion, as it can never give a greater alkalinity to the hot boiler water than about 6° . If at any time the amount of the caustic soda gets inconveniently high, part of it can easily be got rid of by the blow-off cock. It would here be as well to point out that it is much better not to blow off until the boiler water has acquired a considerable concentration and then to blow out, say, 6 or 8 inches. This is better than blowing off, say, 1 inch per day, for it gets rid of a larger quantity of a stronger solution and is more effective in reducing the strength.

The following is an example from actual practice :—

<i>Town Water</i>	
Silica	·24
Oxide of Iron	·10
Sulphate of Lime	6·73
Carbonate of Lime	16·09
Nitrate of Lime	3·04
Sulphate of Magnesia	2·94
Nitrate of Sodium	1·90
Chloride of Sodium	5·73
	<hr/>
	36·77
	<hr/>
Hardness	25·35°
Free Carbonic Acid	8·32 grains per gall.
„ Oxygen	30·82 c.c. „ „

After treatment with calcium hydrate and soda ash it contained :—

<i>Treated Water</i>	
Silica	·10
Oxide of Iron	·06
Calcium Hydrate	5·40
Caustic Soda	1·33
Nitrate of Sodium	5·06
Sulphate of Sodium	9·55
Chloride of Sodium	5·73
	<hr/>
	27·23
	<hr/>
Hardness	7·30°
Free Carbonic Acid	nil
„ Oxygen	30·82 c.c. per gall.

The original hardness has been destroyed and the water re-hardened to $7·3^{\circ}$, and the whole of this hardness is due to calcium hydrate.

The Works test of this sample of treated water gave :—

Hardness (Soap)	7.0°
Alkalinity to Phenolphthalein	9.0°
„ to Methyl Orange	9.2°

When diluted with nine times its volume of condensed water the tests were :—

Hardness	.8°
Alkalinity to Phenol	.9°
„ to Methyl Orange	1.0°

These tests were made on 70 c.c. of the water, using N/50 Solutions.

After steaming 672 hours the boiler water contained :—

Boiler Water

Calcium Hydrate	3.40
Caustic Soda	84.70
Nitrate of Sodium	119.00
Sulphate of Sodium	275.08
Chloride of Sodium	159.70
	<hr/>
	641.88
	<hr/>

which is a concentration of 280. The boiler-water is in good condition and the alkalinity not excessive. The boiler was easily run for over 1000 hours by a moderate use of the blow-off cock; especially on the Sunday morning, when it was possible to blow down some 9 or 10 inches, and this blow off did much more good than blowing off a little each day.

This treatment put the condensate into good condition, and the corrosion which had taken place in the economizers previous to this treatment was entirely stopped. A test made on the Air Pump discharge water showed :—

Mineral Matter	nil
Free Acid	nil
„ Oxygen	32.4 c.c. per gall.

so that there was no doubt about the free acid being entirely eliminated. These tests were made when the make-up was 10 per cent. This was afterwards reduced to 3 per cent., and the feed water going into the boilers gave the following tests :—

Hardness	.2°
Alkalinity to Phenolphthalein	.3°
„ to Methyl Orange	.4°

These are the ideal figures which should be aimed at in treating the water for boiler feed.

This boiler was run continuously for nineteen months without cleaning. The blow-off cock was used every Sunday morning to keep down the concentration of the boiler water, and the boiler was emptied each time it was laid off for "sooting," but no cleaning was done. After 13,100 hours' steaming, during which time 16,500,000 gallons of this feed water was evaporated, the lower tubes were found to contain a scale $\frac{1}{16}$ inch thick. This scale had the following composition :—

Silica	·62
Oxide of Iron	1·52
Sulphate of Lime	33·66
Carbonate of Lime	26·63
Calcium Hydrate	35·52
Magnesia	2·05
	<hr/>
	100·00
	<hr/>

As this was the first long run made at this station with the water treated in this way, even better results may be anticipated. The treatment also entirely arrested the corrosion in the economizers.

The Hardness should always be slightly less than the alkalinity. This shows that there is a slight soda alkalinity going forward into the boilers, and it is an alkalinity which it is necessary to maintain. The alkalinity to Methyl Orange should be the same as that to Phenolphthalein, but owing to the fact that Methyl Orange is a less delicate indicator than Phenolphthalein it always gives slightly higher figures in practice. When the two alkalinities are the same it shows that all the alkalinity is caustic. If in practice it is found that the feed water gives a considerably higher reading to Methyl Orange than to Phenolphthalein, then the condensate must have contained some free carbonic acid (owing to leaky condensers or other cause) and this is being tackled by the caustic alkalinity in the treated water.

If the tests show that the Hardness is greater than the alkalinity, the permanent hardness in the original hard water has not been destroyed and scale-forming matter (most probably sulphate of lime) is going forward into the boilers. This should be corrected at once by using a little more soda ash in the mixture for treating the hard water.

The principle of this method is first to entirely destroy the

hardness of the water used for make-up, and at the same operation to reharden it to the necessary degree with calcium hydrate and give it in addition a slight soda alkalinity.

When the calcium hydrate is in excess, the soda ash is converted into caustic soda, and goes forward as such. Some steam users are somewhat timid of caustic soda, but this need not be the case, for whether the soda goes into high-pressure boilers as carbonate or caustic, the result is the same. The carbonate is converted into caustic with the elimination of some acid which gets into the steam and has to be stopped in its next passage through the hot well. Fortunately the method of treatment advocated precludes the possibility of carbonate of soda going into the boilers, for if it is attempted to put in any great quantity, the hardness of the mixed feed will be totally destroyed and the tests will show high alkalinity both to Phenolphthalein and Methyl Orange.

A sample of feed water treated in this way gave the following tests :—

Hardness	·8°
Alkalinity to Phenol	·5°
„ to Methyl Orange	·6°

Here the Hardness is considerably greater than the alkalinity, there is therefore some scale-forming material going forward.

A full analysis of the water was made and gave the following results :—

Treated Feed Water

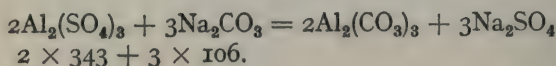
Calcium Hydrate	·31
Sulphate of Lime	·51
Nitrate of Sodium	·20
Sulphate of Sodium	·05
Chloride of Sodium	·40
								<hr/>
								1·47
								<hr/>

Which confirms the conclusion drawn from the tests that there is scale-forming material going forward and that there is a deficiency of soda.

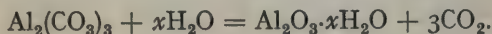
Condensed waters frequently contain oil, and it is necessary to remove this before the condensed water is pumped back into the boilers. This removal is usually brought about by the use of sulphate of alumina in some shape or form, usually in the form of alumina ferric, an impure sulphate of alumina containing a

little ferric sulphate. Alumina ferric generally contains 16 per cent. of alumina, which is equal to 53 per cent. of sulphate of alumina, the remainder being water. Alumina ferric is often acid, but is also supplied as a basic salt. In this form a slight excess of the bauxite or alum shale has been used, and the salt is not entirely soluble. The free acid, however, is destroyed, and the alumina solution does not have such a destructive effect upon the measuring valves and vessels containing it.

When sulphate of alumina is brought into contact with a solution of carbonate of soda, a gelatinous precipitate is formed, thus :—



The carbonate of alumina so formed immediately breaks up into hydrate of alumina and free carbonic acid :—



The gelatinous precipitate of alumina unites with any oil that may be suspended in the condensed water, and enables it to be easily filtered and freed from oil.

Twice 343 parts of real sulphate of alumina require 3×106 (318) parts of soda ash to decompose it, but as alumina ferric only contains about 50 per cent. of sulphate of alumina, 343 parts require 318 parts soda ash, and as it is always advisable to have a slight excess of soda it is best to use equal weights of the two materials. This will ensure the complete precipitation of the alumina and at the same time give a slight soda alkalinity to the treated water. The actual amounts necessary for each 1000 gallons of condensed water will depend upon the amount of oil contained in the water, but seldom amounts to more than 4 oz. per 1000 gallons.

The objection to this method is the setting free of all the carbonic acid in the carbonate of soda used to precipitate the alumina. As carbonate of soda contains about 40 per cent. of carbonic acid, each lb. of soda ash will set free 40 lb. or 2800 grains of carbonic acid. This will mean that every 1000 gallons of the treated water would contain 2.8 grains of free carbonic acid, a quantity which, as is shown elsewhere, would have a very corrosive action on the economizers. If less than 1 lb. is used

the amount of free carbonic acid would be proportionally less. The following is an example from actual practice :—

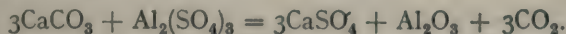
<i>Condensed Water</i>				
Free Oxygen.	.	.	.	29.25 c.c. per gall.
" Carbonic Acid05 grains "
Oil78 " "

<i>Treated Water</i>				
Free Oxygen	.	.	.	29.47 c.c. per gall.
" Carbonic Acid.65 grains "
Oil	.	.	.	nil

The quantities of alumina and soda ash used were not given with the samples, but apparently about 4 oz. of soda ash had been used per 1000 gallons.

This difficulty can be got over by using caustic soda instead of soda ash. By this means the alumina is directly precipitated as hydrate without the intermediate carbonate stage, and there is no carbonic acid to be set free. Care must, however, be taken not to use too much caustic soda, as the precipitate is soluble in excess and the alumina would be redissolved and not do its work in eliminating the oil. As 80 parts of caustic soda are equivalent to 106 parts of carbonate of soda, the quantity of caustic required would be roughly four-fifths of the weight of the alumina ferric used.

Carbonate or bicarbonate of lime will also precipitate the alumina from the sulphate, and this reaction is sometimes utilized by using a hard carbonate water as the precipitating medium. This is, however, objectionable from the boiler point of view, however promising it may be from the point of view of saving the cost of soda and therefore cheapening the de-oiling process. In this case not only is carbonic acid set free to cause corrosion in the economizers, but sulphate of lime is also formed and will cause a hard scale.



Another method of eliminating the oil is to pass the oily water through tanks in which an electric current is passed. At one electrode hydrated ferric oxide is liberated, and this plays the same part as precipitated alumina in collecting and retaining the oil, and the treated water is easily filtered quite clear and free from oil.

The following is an example from a plant capable of dealing with 1000 gallons of oily water per hour.

The oily water contained 3.64 grains of oil per gallon, and was quite milky. After passing through the cell and filter it was quite clear and free from oil. The mineral constituents were :—

De-oiled Water

Silica08
Oxide of Iron16
Sulphate of Lime	1.92
Carbonate of Lime	3.27
Chloride of Magnesia86
Chloride of Sodium	1.39
	<hr/>
	7.68
	<hr/>
Hardness	5.50°

These figures show that in this instance about 20 per cent. of hard water had been added to the oily water to obtain the necessary conductivity for the current. A sample of the oily deposit was collected at the same time and found to contain :—

Oily Deposit

Hydrated Ferric Oxide	43.58
Oil	54.52
Water	1.60
	<hr/>
	99.70
	<hr/>

The ferric hydrate has collected about $1\frac{1}{4}$ times its weight of oil, and if the ferric hydrate is calculated back to metallic iron, this would mean that each part of iron corroded in the cell collects and removes about $2\frac{1}{2}$ times its own weight of oil.

The objection to this method is, of course, the use of hard water to allow the passage of the current, but this could no doubt be got over by the use of softened water, or by adding salt or sulphate of soda.

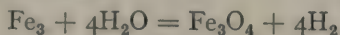
Any method of removing the oil necessarily implies the addition of some material to the water. In the alumina method an alkali is added to precipitate the hydrate of alumina, and in the electric method something has to be added to the water to render it sufficiently conductive to allow the current to pass and form the precipitate of hydrated oxide of iron.

CHAPTER XIII

THE SUPERHEATER

THE superheater is an arrangement of pipes through which the steam has to pass after it has left the boiler and before it reaches the steam pipes proper. It is placed in the exit gases from the furnace, and as these gases are generally at a temperature of over 600° F. the steam inside the pipes is raised in temperature and any moisture it may have contained is converted into dry steam. In this way the temperature of the steam can be raised at least 100° F., and the steam coming from the superheater of a boiler working at 200 lb. pressure will have a temperature of 500° F. and often considerably higher.

At this temperature steam is decomposed by metallic iron according to the equation



hydrogen being given off and magnetic oxide of iron formed. By this reaction the superheater tube is generally lined with a film of this magnetic oxide. A sample of this lining yielded the following figures:—

Silica	·12
Ferrous Oxide	17·34
Ferric Oxide	82·56
	<hr/>
	100·02
	<hr/>

This is the normal film formed in superheaters by the action of pure steam. The film is adherent to the metal and protects it from further action so long as the steam is not contaminated with other bodies liable to cause corrosion.

The following is another analysis of a deposit taken out of a superheater tube.

Superheater Deposit

Silica	·40
Ferrous Oxide	14·40
Ferric Oxide	84·66
	<hr/>
	99·46
	<hr/>

The analysis of this deposit does not differ sensibly from the last analysis, but in this case the deposit was of a totally different nature, and was produced by the almost total disintegration and corrosion of the tube. The corrosion was so bad in places that the tube was perforated. In the former case the superheater tube was merely coated by an adherent and hard protective coating of the oxide, in the latter the tube was almost entirely converted into a loose mass of the oxide. This oxidation had been brought about by the steam in the presence of hydrochloric acid, and the hydrochloric acid had found its way into the superheater from the decomposition of some chloride of magnesia carried up from the boiler water. The hydrochloric acid had dissolved up the iron to form chloride of iron and so destroyed the tube, and the chloride of iron so formed had been converted into oxide of iron by the steam, and the hydrochloric acid liberated to attack more iron.



Steam as a rule contains some carbonic acid, and at the temperature of the superheater the hydrogen liberated by the action of iron on steam reduces carbonic acid to carbon monoxide. This carbon monoxide in contact with the magnetic oxide reduces some of it to metallic iron, reforming carbonic acid. The action is reversible and the carbonic acid is again reduced by metallic iron, and so the process goes on through the whole length of the superheater tubes. These reversible actions are somewhat complicated, but seem to prevent the superficial layer of magnetic oxide from attaining any appreciable thickness. The ultimate fate of the carbonic acid is somewhat obscure, but it does not seem to leave the superheater as carbonic acid, but rather as some other carboxylic acid.

This acid sometimes shows the properties of formic acid, whilst at other times it is left as a gummy mass when the condensed water is evaporated to dryness. The quantity is very small but quite sufficient to convey acid properties to the condensed water, and render it corrosive to iron and steel.

Occasionally some of the boiler water is carried into the superheaters and causes the tubes to become choked and sometimes quite blocked up. When the boiler waters contain an insoluble sludge owing to imperfect softening, or to no treatment at all, this sludge is sometimes caught up by the rush of steam and deposited in the superheater tubes, and at the temperature

sometimes reached, the carbonate of lime in the current of steam loses its carbon dioxide and becomes converted into free lime. The following analyses illustrate this action. One is the analysis of the sludge found in the steam drum prior to its entrance into the superheater, and the other an analysis of the deposit actually taken out of the superheater.

Steam Drum Deposit

Silica	2.70
Ferric Oxide	1.24
Sulphate of Lime77
Carbonate of Lime	90.86
Magnesia	4.32
	<hr/>
	99.89

Superheater Deposit

Silica	1.08
Ferric Oxide	7.08
Calcium Hydrate	73.26
Carbonate of Lime	7.50
Magnesia	3.24
Sulphate of Sodium	3.91
Chloride of Sodium	2.47
Moisture, etc.	1.46
	<hr/>
	100.00

The carbonate of lime carried into the superheater has been converted into calcium hydrate and carbonic acid given off.



Some of the carbonate of lime found in the superheater was probably produced by exposure to the atmosphere after the piece of tube had been cut out, as the deposit contained much more carbonate at both ends of the piece of tube than it did in the middle where it was less exposed. This is a somewhat unusual deposit, but it illustrates what can happen in the superheaters if the boilers are allowed to prime or froth through soap or saponifiable oils getting into the boiler water. Although it is not a common occurrence to find superheaters blocked in this way by an insoluble lime deposit, soluble soda salts are not infrequently found where frothing has taken place, and for this reason superheater boxes are often provided so that the tubes can be washed out from time to time.

When boiler waters contain nitrates, which is not infrequently the case, any boiler water carried up in this way can cause

extensive corrosion in the superheaters. As the steam becomes dry it drops the nitrates in the form of a solid deposit. These solid nitrates in contact with metallic iron at the superheater temperature are decomposed and nitric acid given off. The nitric acid so liberated, besides affecting the steam and rendering it acid, also attacks the superheaters to such an extent that they become perforated. The following is an analysis of a deposit which had been formed in this way, and the superheater badly corroded.

Superheater Deposit

Silica	2.02
Ferrous Oxide	12.82
Ferric Oxide	69.20
Ferrous Chloride	1.27
Sulphate of Lime	1.12
Carbonate of Lime	6.40
Magnesia23
Chloride of Sodium	2.34
Moisture, etc.	4.60
	<hr/>
	100.00
	<hr/>

This is principally oxide of iron and contains no nitrates, although the boiler water contained 11.25 grains of nitrate of lime and 8.40 grains of nitrate of sodium per gallon.

Boiler waters which contain chloride of magnesium or sea-water if carried into the superheaters cause very rapid corrosion, owing to the liberation of hydrochloric acid. The chloride of magnesium is first deposited in the dry form, and this by further heating in contact with metallic iron splits up into magnesia and hydrochloric acid. This action can easily be illustrated by dropping sea-water on to a hot iron plate. A white deposit is formed and much acid given off. If the iron plate is quite bright the deposit is of a greenish colour owing to the formation of ferrous oxide. In the superheater the steam is always well charged with free oxygen, and this oxygen converts the bulk of the ferrous oxide so formed into ferric oxide as shown in the accompanying analysis of a deposit formed in this way.

Silica20
Ferrous Oxide	15.84
Ferric Oxide	82.92
Magnesia21
Chloride of Sodium29
	<hr/>
	99.46
	<hr/>

In the following case the analyses show the effect of bad practice in treating the water and of allowing the boiler water to contain soap.

Boiler Water

Caustic Soda	199.58
Carbonate of Sodium	463.60
Sulphate of Sodium	2147.75
Chloride of Sodium	1719.90
Soap	10.70
	<hr/>
	4541.53
	<hr/>

Drum Deposit

Silica	8.16
Alumina and Oxide of Iron	20.48
Carbonate of Lime	60.14
Magnesia	8.96
Organic Matter, etc.	2.26
	<hr/>
	100.00
	<hr/>

Superheater Deposit

Silica	1.90
Oxide of Iron20
Carbonate of Lime	90.43
Magnesia	6.77
Moisture, etc.70
	<hr/>
	100.00
	<hr/>

At the temperature reached in the superheater and in a current of steam, reactions take place quite different to those which take place in the boiler, and a water which gives an alkaline reaction in the boiler can develop acid in the superheater.

The water found in the superheater boxes sometimes attains a very considerable concentration. The following is an example taken from a superheater box. This boiler was evaporating softened London Main water.

Water from Superheater Box

Caustic Soda	41.10
Carbonate of Soda	133.56
Sulphate of Sodium	2062.73
Chloride of Sodium	1105.65
Nitrate of Sodium	traces
	<hr/>
	3343.04
	<hr/>

CHAPTER XIV

PRIMING

PRIMING is a condition in which liquid water leaves the boilers with the steam, and this water is quite distinct from that always carried away in saturated steam. One of the requirements of a perfect steam boiler is the generation of commercially dry steam at all rates of evaporation, and different types of boilers at low or normal evaporation will generate fairly dry steam, but under hard-working or forced conditions will prime or tend to prime, and the percentage of water in the steam will be objectionably high. This tendency to prime may be due to some of the constituents in the boiler water, to insufficient or poor circulation, insufficient steam disengaging surface or insufficient space between the disengaging surface and the point of outlet for the steam.

The moisture held in suspension by saturated steam is held in the same way as any other gas would hold moisture, but the water due to priming is additional to this and is due to some physical condition rather than to a chemical one.

In marine boilers priming may be due to violent alterations in the boiler water level owing to rolling or pitching whereby in the absence of dry pipes or other suitable arrangement, water may be trapped between the steam outlet and the normal working level, and forced into the steam pipes in the liquid state. Priming may also be produced by sudden variations in the evaporation owing to changes from half speed to full speed, and by the sudden opening of a large valve it is possible to practically empty a boiler of its contents.

Superheaters are designed to convert the moist steam into dry steam, and if this saturated steam contains boiler water, the dissolved solids in the boiler water will be deposited in the superheaters and soon block them up. Although superheaters are occasionally blocked in this way, it is rather unusual and shows that priming is an abnormal condition.

Water deposited in steam pipes where priming has taken place

contains the soluble salts contained in the boiler water, showing that the boiler water itself has passed away with the steam. Water condensed from saturated steam, where no priming has taken place, contains nothing but gases and no mineral matter whatever, showing that the extra moisture in the steam has not passed from the boiler in the liquid state but as a vapour.

The following is the analysis of a sample of condensed steam :—

Condensed Steam (Priming)

Nitrate of Sodium	17.85
Sulphate of Sodium	131.35
Caustic Soda	10.08
Carbonate of Soda	107.40
Chloride of Sodium	122.85
	<hr/>
	389.53
	<hr/>

Free Oxygen 33.97 c.c.

There can be no doubt that priming has taken place in this case. It is certainly a very bad sample, but is given to illustrate the difference between the water carried up by priming and the normal moisture carried up by saturated steam.

Condensed Steam (no Priming)

Mineral Matter	nil.
Organic Matter56 grs. per gall.
Free Oxygen	26.10 c.c. " "
Free Acid calculated as Carbonic Acid	15.12 c.c. " "

Where priming has taken place it has sometimes been associated with a high alkalinity in the boiler water, and it has therefore been assumed that alkalinity is the cause of priming. There is no prima facie reason at all why alkalinity should cause priming any more than a correspondingly concentrated solution of sulphate of soda or common salt.

There are many thousands of boilers working with very considerable quantities of all three of these salts in solution, where priming is unknown.

The following are two typical instances :—

Boiler Water No. 1

Caustic Soda	85.40
Carbonate of Sodium	5.94
Nitrate of Sodium	19.34
Sulphate of Sodium	209.45
Chloride of Sodium	106.48
	<hr/>
	426.61
	<hr/>

Boiler Water No. 2

Calcium Hydrate	5.18
Caustic Soda	120.96
Nitrate of Sodium	160.65
Sulphate of Sodium	253.52
Chloride of Sodium	208.84
	<hr/>
	749.15
	<hr/>

With the exception of a little calcium hydrate contained in No. 2 Boiler Water, these waters contain practically the same materials, and if either alkalinity or concentration had anything to do with the priming, No. 2 should cause more priming than No. 1, both boilers being water-tube boilers of the same type, and if there was any difference at all in the working, No. 2 was worked harder than No. 1.

In point of fact, No. 1 water primed badly and No. 2 did not prime at all. Although these analyses as recorded give no clue to the cause, further investigation showed that No. 1 water contained 3.64 grains of soap per gallon, whilst No. 2 was quite free from soap. It was this soap in No. 1 water which caused the priming or frothing, and so allowed the boiler water to be caught up with the steam. On shaking this water in the bottle containing it, a lather was formed which persisted for a minute or two. This shaking test often furnishes a rough-and-ready test for the presence of soap in boiler waters. Sometimes the lather will persist for many minutes, at others it disperses in a very short time, but is still visible when the bottle is shaken.

The following are other examples:—

Non-Priming Boiler Water

Calcium Hydrate	6.93
Caustic Soda	119.30
Nitrate of Sodium	297.50
Sulphate of Sodium	299.94
Chloride of Sodium	409.50
	<hr/>
	1133.17
	<hr/>

Priming Boiler Water

Aluminate of Soda	5.93
Caustic Soda	203.00
Carbonate of Sodium	125.12
Nitrate of Sodium	29.75
Sulphate of Sodium	510.96
Chloride of Sodium	278.46
Soap	5.12
	<hr/>
	1158.34
	<hr/>

Non-Priming Boiler Water

Calcium Hydrate	6.95
Caustic Soda	21.90
Nitrate of Sodium	1.19
Sulphate of Sodium	21.74
Chloride of Sodium	23.34
	<hr/>
	75.12
	<hr/>

Priming Boiler Water

Calcium Hydrate	2.59
Caustic Soda	5.38
Nitrate of Sodium	4.46
Sulphate of Sodium	61.39
Chloride of Sodium	53.23
Soap	7.17
	<hr/>
	134.22
	<hr/>

The amount of soap was calculated from the estimated fatty acids, on the assumption that pure soap contains 70 per cent. of fatty acids.

Many other instances could be given, but these are sufficient to show that in many instances soap may be an unsuspected cause of priming or foaming. A small quantity of soap might easily be missed in making an analysis of a boiler water unless it were specially looked for. In cases where the foaming has been attributed to sewage, it is more than likely that the sewage contained soapy matters. The soap is, however, in most cases due to the oil used in lubricating the condensing engines and gets into the boilers with the condensate.

In a secondary sense alkalinity might be blamed for the priming, for had there been no alkali in the boiler water no soap would be formed. Neither chloride nor sulphate of sodium would have formed a soap, and there would have been no priming. In *this* sense alkalinity may be said to cause priming, but this is rather straining the point, as alkali should be present in the boiler water and oil should not, and it is hardly fair to say that because saponifiable oil gets into the boiler, alkalinity is responsible for the priming.

In addition to the loss of heat caused by priming and the damage to the engines which this water can bring about, the superheaters themselves can be blocked up by solid deposits brought in this way from the boilers. They can also be eaten away by the corrosive acids developed by certain boiler waters

when they are desiccated by superheating. Examples of this are given in the Chapter on the Superheater. Not only is the temperature of the superheater higher than that of the boiler, but the steam as it becomes dry must deposit these solids from the boiler water, and instead of a comparatively weak solution of these salts becoming exposed to the boiler temperature, the dry solids themselves are exposed to the superheater temperature in a current of superheated steam. The chemical reactions that will thus take place in the superheater are quite different from those taking place in the boiler. For instance, any chloride of magnesia which gets into the superheater will develop hydrochloric acid, and this acid in the form of gas will rapidly corrode the iron. A mixture of sulphate of magnesia and chloride of sodium will also do this. Nitrate of lime and nitrate of magnesia will develop nitric acid or nitrous acid, and these acids will also cause corrosion in the superheaters and contaminate the condensate. Even nitrate of sodium, which may be innocuous in the boiler water, is decomposed when heated in the dry state in a current of superheated steam. It is not necessary that the boiler water should be concentrated in order to bring about this form of corrosion, for any solution containing these salts, however dilute, must necessarily be desiccated and deposited in the solid form in the superheater.

CHAPTER XV

EXTERNAL DEPOSITS

WHEN in hand firing a fresh charge of coal is spread over an incandescent fire bed, the charge is rapidly heated, and the more volatile constituents in the coal are promptly distilled off and pass into the combustion space proper, where, mixing with an excess of air, they are more or less completely burnt. The residue left on the grate is mostly an incandescent mass of carbon or coke.

The oxygen in the air, passing through the grate bars, combines with the first incandescent carbon encountered and forms carbonic acid (CO_2), and then in passing through upper layers of hot coke or coal, an additional molecule of carbon is absorbed and carbon monoxide (CO) is formed.

Owing to the high temperature of the fuel bed, this action takes place even if the bed be quite thin, say 3 inches to 4 inches, in fact, speaking generally, it would be necessary to reduce the thickness to 2 inches or under to prevent this action taking place. Hence the necessity of supplying additional air through fire doors, or other openings to secure complete combustion on an ordinary hand-fired grate.

The same remarks apply to the mechanical firing of coal, but with mechanical stokers, particularly those of the self-cleaning or self-clinkering type, there is usually a sufficient passage of air through the clinker bed to provide the excess required.

The process is really similar to that of gasifying fuel in a gas producer, but in the latter the temperature is comparatively low, and it is necessary to have a deep bed of fuel to prolong the period of contact between the carbonic acid and the hot coke in order to form a maximum quantity of carbon monoxide.

Carbon, as above stated, is in excess in the fuel bed, both with hand or mechanical firing, and it is not until the combustion chamber proper is reached, that an excess of oxygen is present. Under the above conditions a very powerful reducing agent is at work to act upon any reducible and volatile metals in the

ash constituents of the coal, and as these nearly always contain a certain percentage of alkali metals, the latter are reduced from their salts, and being very volatile, pass forward into the combustion space with the other combustible gases. This action is exactly analogous to the method formerly adopted for the manufacture of potassium and sodium, that is, by mixing their carbonates with an excess of carbon or carbonaceous matter and distilling off the metals in retorts. Sodium, and occasionally potassium, is nearly always found in the ash constituents of coal, the consequence being that when such coal is burnt in a boiler furnace, the sodium is always volatilized and passes into the combustion space.

At the same time coal always contains sulphur, generally as pyrites, less frequently and in lesser quantity as sulphate of lime, and some of this sulphur is also distilled off with the other volatile coal gases.

It may be taken that coal contains on an average at least 1 per cent. of sulphur, that is, 22.4 lb. per ton. The amount of alkali metals in the ash constituents is, as a rule, small, but in most coals it amounts to 3 per cent. or 4 per cent. of the weight of the ash, so that if the coal contains 10 per cent. of ash constituents, the percentage of sodium oxide in the coal will be about .3 per cent.—that is, 6.72 lb. per ton of coal; and in poor coals containing 30 per cent. of ash—the amount of sodium oxide might reach nearly 20 lb. per ton of coal burnt. The above figures are merely illustrative and are well within the mark for certain classes and qualities of coal, and are given to show that there may always be a considerable amount of these elements passing into the combustion chamber.

Some coals also contain traces of lead, copper, zinc, bismuth, silver, etc., and these metals being easily reducible by carbon and more or less volatile, are occasionally found in the flue dust or deposits produced from coals.

When the fuel gases pass into the combustion chamber, there is an excess of oxygen, and not only do these gases burn, but the sulphur and volatilized metals also burn and combine with the oxygen, forming oxides of sodium, potassium, etc., and sulphuric acid. A portion of the oxide of sodium unites with the sulphuric acid to form sulphate of sodium, which being a comparatively infusible salt, condenses upon the first cold surfaces in its track, and as in the case of a steam boiler, the flow of gases is designed to impinge upon the boiler plates and tubes—a portion of the

sulphate of soda is deposited thereon, while any portion which has condensed upon particles of ash entrained by the rush of the gases is carried on and deposited upon the economizer tubes or in the flues.

The white deposit generally seen on boiler plates and tubes is sulphate of sodium formed in this way, and so long as it is not allowed to unduly accumulate and melt, it does no particular harm. So long as the boiler-heating surface is kept comparatively cool by the heat being carried away as fast as it is transmitted by the furnace, the sulphate of soda deposit merely acts as a hindrance to the heat transmission; but if from an accumulation of oil, internal scale or other cause, the water on the inside of the vessel does not carry away the heat as fast as it is generated, the temperature of the boiler-heating surface rises, and if it reaches 1700° F., the sulphate of soda melts and has a very rapid and destructive action upon the metal forming the heating surface.

Melted sulphate of soda gives up oxygen to iron and converts it into magnetic or scale oxide, forming a "Scab" on the surface. This weakens the metal at this point, and the natural working of the structure, due to expansion and contraction following variations in gas temperatures and rates of water evaporation, has the effect of periodically scaling off the "Scab," and of leaving a clean fresh surface of iron for a repetition of the process. The parts thus affected obviously become weaker and weaker, the action being accelerated by the stress to which the parts are subjected from the internal steam pressure, and a bulge is the natural result.

It is in this way that many of the tubes which fail in Water Tube Boilers are destroyed. They are actually burnt, not by the oxygen in the flue gases, but by means of the oxygen supplied by the adherent plaster of sulphate of soda. They are destroyed at a very much lower temperature than could possibly be the case if they were merely burnt by atmospheric influences, and in at least nine cases out of ten, the failure is due to external conditions.

The following are typical analyses of this kind of deposit:—

External Deposits

Silica	5.32
Ferrous Sulphate	6.08
Ferric Sulphate	20.50
Sulphate of Sodium	65.10
Moisture, etc.	3.00
	<hr/>
	100.00
	<hr/>

Silica	4.61
Ferric Sulphate	11.07
Sulphate of Sodium	84.32
	<hr/>
	100.00

" Scab "

Silica, etc.	7.94
Ferrous Oxide	52.70
Ferric Oxide	39.36
	<hr/>
	100.00

Ratio of Iron to Oxygen = 2.9 : 1

ACID SULPHATES OF SODA DEPOSITS

As the sulphuric anhydride (SO_3) in the furnace gases is generally much in excess of the sodium oxide, the sulphate of soda so formed sometimes carries down with it an extra quantity of the sulphuric anhydride in the form of the double salt $\text{Na}_2\text{SO}_4 \cdot \text{SO}_3$. The conditions and temperature at which this salt is deposited are not exactly known, but the general tendency is for it to be deposited in the comparatively cool parts, rather than on to those parts subject to the greatest heat. In the same boiler, it is sometimes found that whilst the deposit on the hottest parts is quite neutral, the deposit on the cooler parts is distinctly acid. This double salt is hygroscopic and when cold absorbs moisture to form the acid bisulphate.



When sufficient moisture has been attracted, the deposit attacks the iron, and this is the reason why the white external deposit soon turns yellow when the tubes are thrown on to the scrap heap and exposed to the weather.

The deposit upon the economizer tubes consists largely of the acid bisulphate, owing to the fact that they are much cooler and at a temperature below the condensing point of sulphuric acid. This admits of the acid bisulphate being deposited directly upon them without the intervention of any moisture except that obtained in the flue gases. Whilst hot this deposit has little if any destructive effect upon iron, but as it is very hygroscopic it attracts water and then has a very corrosive action upon iron, forming a mixture of ferric and ferrous sulphates, and the colour changes to yellow tinged with green, quite unlike the original white deposit. Its most destructive action probably

takes place when the boilers are standing idle. So long as the deposit is warm and dry little or no corrosion will take place, but if it be allowed to attract moisture, either from too low a gas temperature, by sweating of the economizer tubes or by any accidental leakage, rapid corrosion will ensue. Thus it is the economizer tubes next to the cleaning and access doors where moist air can leak in, and those tubes which receive the coolest feed water, that are most subjected to corrosion. In the body of the tubes where it is drier and hotter the action is less. It is this acid deposit which burns the workmen's clothes and hands, as it frequently contains as much as 20 per cent. of active sulphuric acid.

Examples :—

(1)	
Ash	56.70
Ferrous Sulphate46
Ferric Sulphate	16.30
Sulphate of Zinc	1.11
Sulphate of Lime	3.90
Sulphate of Ammonium	5.69
Sulphate of Sodium	3.30
Free Sulphuric Acid	12.54

100.00

(2)	
Ash	68.43
Ferrous Sulphate	1.22
Ferric Sulphate	9.80
Sulphate of Zinc71
Sulphate of Lime	5.83
Sulphate of Ammonia	4.90
Free Sulphuric Acid	9.11

100.00

(3)	
Ash	21.19
Unburnt Carbon	5.71
Ferrous Sulphate	4.85
Ferric Sulphate	34.50
Sulphate of Sodium	2.87
Free Sulphuric Acid	13.33
Moisture, etc.	17.55

100.00

BIRD'S NESTING

From the foregoing it will be seen that the gases in the combustion chamber always contain sodium in the state of vapour, and that this sodium on becoming converted into sodium oxide

and subsequently into sulphate of soda is partly deposited on the heating surfaces, partly carried onwards with the flue dust, and partly deposited upon the brickwork. This brickwork or fireclay is infusible by reason of its freedom from alkalis. In the heated state it is particularly amenable to the action of an alkali oxide such as sodium oxide. The result is the formation of a fusible clay or slag, and the firebricks are gradually destroyed, as is seen by the glazed appearance of the walls of the furnace. The same action takes place in coke ovens, the firebrick being rendered superficially fusible by the action of the sodium oxide on the silica. Where the ash of the coal is fine and light and does not readily clinker, small particles of the light ash are caught up by the current of air in the combustion chamber, and as they consist principally of silica, they become superficially coated with a readily fusible skin of silicate of soda. At the temperature of the furnace this is sticky and plastic, and the particles agglutinate together and build up the formation known as "bird's nesting." This formation gradually blocks up the space left for the passage of the gases, and renders it necessary to remove the "bird's nesting" fairly frequently to preserve a free draught.

Just as water renders clay plastic at ordinary temperatures and enables the swallow to build its nest with moist clay, so does sodium oxide at a high temperature render the ash plastic and binding and enables it to be deposited by a current of gas on heated surfaces.

Bird's Nesting Deposit

Silica	49.78
Alumina and Oxide of Iron	35.84
Lime	8.56
Sodium Oxide	5.70
	<hr/>
	99.88
	<hr/>
Silica	65.16
Alumina and Oxide of Iron	25.12
Sulphate of Sodium	5.47
Sodium Oxide	4.20
	<hr/>
	99.95
	<hr/>

Coals sometimes contain traces of lead ores. Lead being a comparatively volatile metal is volatilized from these coals in the same way as sodium and deposited on the tubes as oxide

and sulphate of lead. Sulphate of lead melts at about 1100° F. and causes the destructive action on the iron at a much lower temperature, as it not only supplies the iron with oxygen, but the reduced lead probably also forms an alloy with the iron and diminishes its power to withstand the pressure.

The following is an analysis of the white deposit on the underneath or fire side of the tubes.

White Deposit

Ash	32.36
Ferrous Sulphate	1.52
Ferric Sulphate	14.80
Sulphate of Lime	2.83
Sulphate of Lead	2.44
Sulphate of Sodium	45.07
Loss, etc.98
	<hr/>
	100.00
	<hr/>

This deposit consists principally of sulphate of soda mixed with fine particles of ash entangled in it. The presence of the sulphate of iron shows the incipient action of this deposit in attacking the iron to form sulphates of iron. The next analysis is a sample of a brown deposit taken from the same tube at a point where it was beginning to bulge.

Brown Deposit

Ash	28.31
Ferrous Oxide	3.49
Ferric Oxide	39.40
Ferrous Sulphate	1.81
Ferric Sulphate	2.70
Sulphate of Lime	1.01
Sulphate of Sodium	22.72
Loss, etc.56
	<hr/>
	100.00
	<hr/>

Here the sulphate of soda has fallen 50 per cent. and the fusible sulphate of lead has also disappeared, and over 40 per cent. of oxide of iron has come in. The sulphates of soda and lead have given up oxygen to the iron, and in doing so have been converted into oxides which being very fusible have dropped off and fallen back into the furnace and probably helped to form a fusible ash to attack the firebars. This analysis marks a distinct stage in the process of disintegration. The next stage where the whole of the sulphate of soda has disappeared is

DEPOSITS FROM COKE OVEN GASES

Silica	3.98
Oxide of Iron	20.36
Sulphate of Sodium	45.14
Moisture, etc.	3.60
Unburnt Carbon	26.92
	<hr/>
	100.00
	<hr/>

The presence of unburnt carbon shows that insufficient air has been used in burning the gases, and the result of this incomplete combustion is shown in the next analysis, which is an analysis of the "Scab."

" Scab "

Silica44
Ferrous Oxide	39.20
Ferric Oxide	16.02
Ferrous Sulphide	36.44
Sulphate of Sodium	6.48
Undetermined, etc.	1.42
	<hr/>
	100.00
	<hr/>

The ferrous sulphide has been produced by the sulphuretted hydrogen in the coke-oven gases. The amount of air used had either not been sufficient or the flame had been allowed to impinge too closely on to the iron. Under these circumstances the sulphur, which would be the last to burn, would be brought into direct contact with the heated iron and would form the fusible ferrous sulphide. The method of burning sulphuretted hydrogen in an insufficient supply of air is made use of industrially in the recovery of sulphur from gases containing sulphuretted hydrogen. The hydrogen burns to water, whilst the sulphur is deposited on the walls of the combustion chamber.

EXUDATIONS

When the boiler water becomes concentrated or contains certain salts, it often finds its way through the joints or seams of the boiler, the manhole joints or handhole doors, or through the glands of the water-gauge cocks. This water, containing much soluble matters, having passed through the joints becomes desiccated on the hot surfaces of the metal and forms unsightly exudations or excrescences, which if left alone or allowed to accumulate often form deposits of considerable magnitude, and

in some installations it is not an uncommon sight to see very considerable masses of these saline deposits on the outside of the boilers. In themselves they are not of much consequence, and unless the leakage is through seams do not do much harm to the boilers, they are more an eyesore than anything else, but they show that the boiler water is not in good condition either through working to too high a concentration or else too alkaline.

The following are analyses of some of these deposits :—

Deposit from Glands of Gauge Cocks

Silica	·94
Alumina	1·18
Carbonate of Lime	3·78
Oxide of Copper	·78
Nitrate of Lime	·94
Nitrate of Sodium	33·94
Sulphate of Sodium	34·15
Chloride of Sodium	23·87
	<hr/>
	99·58
	<hr/>

Manhole Deposit

Silica	·25
Sulphate of Sodium	78·28
Chloride of Sodium	19·89
Moisture, etc.	1·58
	<hr/>
	100·00
	<hr/>

Header Excrescence

Coal, etc.	2·16
Sulphate of Sodium	31·20
Nitrate of Sodium	35·90
Chloride of Sodium	30·74
	<hr/>
	100·00
	<hr/>

Dust, etc.	3·38
Carbonate of Sodium	6·36
Sulphate of Sodium	54·16
Chloride of Sodium	31·59
Moisture	4·28
	<hr/>
	99·77
	<hr/>

Insoluble Matter	1·04
Sulphate of Sodium	56·41
Carbonate of Sodium	2·97
Chloride of Sodium	2·92
Water of Crystallization	36·66
	<hr/>
	100·00
	<hr/>

EXTERNAL DEPOSITS

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Insoluble Matter	1.04
Sulphate of Sodium	10.48
Chloride of Sodium	86.00
Moisture, etc.	2.48

 100.00

Silica70
Nitrate of Sodium	5.35
Sulphate of Sodium	9.42
Chloride of Sodium	84.24

 99.71

CHAPTER XVI

FAILURE OF CLEAN TUBES

IN a modern boiler plant the water is fed into the boilers, where it is evaporated into steam, this is superheated in the superheater, does its expansive work in the engines by parting with most of its heat, the remainder of the heat is removed by condensers and the cooled condensed water is returned to the boiler for re-evaporation.

If there were no loss of steam, the only solid matters would be the original quantity put into the boiler, but as there is always a loss of steam, this loss has to be made good by a make-up water, which will naturally contain more or less solid matter according to the source of supply. The boiler thus becomes the receptacle for all the mineral matters contained in the feed supply, and as time goes on the solids naturally accumulate until a point is reached at which even soluble solids such as sulphate of soda and chloride of sodium will crystallize out.

This time could, of course, be almost indefinitely postponed by reducing the loss of steam to a minimum whereby the amount of make-up is reduced, and by removing a portion of the concentrated solution in the boiler by means of the blow-off cock.

But even then, it is not good practice to work the boiler water to a strength at which soluble impurities are liable to deposit. Sulphate of soda is a salt that develops heat on dissolving in water, and is therefore one of the salts which become less soluble as the temperature rises. On the other hand, chloride of sodium depresses the temperature of the water in which it dissolves, and therefore increases in solubility as the temperature rises. These statements only apply to temperatures up to the boiling point of the saturated solutions of these salts. What happens above these temperatures and in boilers working at high pressures is not exactly known. At low temperatures the curves of solubility are widely apart, and approach one another as the temperature rises up to the boiling point. It is therefore not unreasonable to suppose that at temperatures above the

normal boiling point which are reached in boilers worked at many atmospheres of pressure, these curves will intersect. It is known that sulphate of soda becomes insoluble in water alone at a temperature of 570°F .

As these are the only reliable data bearing on the subject, the following experiments were carried out :—

EXPERIMENTS

(1) A strong solution of rock salt containing 15.66 per cent. of chloride of sodium was shaken up with an excess of anhydrous sulphate of soda and then allowed to stand for 24 hours at a temperature of $59/60^{\circ}\text{F}$. The solution was then found to contain 3.14 parts of sulphate of soda per 100 parts of the solution.

(2) A solution of sulphate of soda containing 8.69 parts per 100 was heated to 140°F . and crystals of chloride of sodium put in so long as they would dissolve. The liquid was allowed to stand for 24 hours at $59/60^{\circ}\text{F}$. There was a considerable crystallization and the clear saturated liquor contained :—

	Per cent.
Sodium Chloride	33.50
Sodium Sulphate	2.56

(3) A strong solution of sodium chloride was boiled and the loss of water made good by adding a solution of sulphate of soda, saturated in the cold. The boiling was continued until crystals made their appearance. These were crystals of sulphate of soda, and the liquid contained :—

	Per cent.
Sodium Chloride	26.20
Sodium Sulphate	6.10

(4) A strong solution of sulphate of soda was boiled and loss made good by adding a strong solution of chloride of sodium. The boiling was continued until crystals were deposited. These crystals were chloride of sodium, and the remaining liquid contained :—

	Per cent.
Sodium Chloride	42.20
Sodium Sulphate	10.98

(5) A solution containing 2.75 per cent. sulphate of soda and 1.09 per cent. of chloride of sodium was evaporated under ordinary pressure until crystals began to be deposited. These were crystals of sulphate of soda, and the solution contained :—

	Per cent.
Sodium Sulphate	21.83
Sodium Chloride	9.07

As the initial ratio of these salts was 2.5 : 1 and the ratio at the end 2.4 : 1 the experiment was stopped just about the point of saturation.

Although there is no close concordance between these results, they prove that sulphate of soda is not nearly so soluble in a solution of sodium chloride as it is in pure water. The solubility of sulphate of soda in water at 60 °F., determined at the same time as these experiments were carried out, was 48.4 parts per 100.

Sulphate of soda has also the somewhat remarkable property of forming supersaturated solutions, and these solutions can be so much supersaturated that they solidify on disturbance or when a crystal of solid sulphate of soda is introduced.

These experiments agree in showing that sulphate of soda is very much less soluble in salt solutions than it is in water, and when this fact is taken in conjunction with the fact that the solubility of sulphate of soda in water diminishes as the temperature rises and becomes insoluble in water alone at 570° F., then there are reasonable grounds for assuming that concentrated boiler waters can deposit sulphate of soda at a very much less density than is usually supposed. It is possible that chloride of sodium may sometimes come out of the solution as shown by the experiments. This, however, will depend upon the relative amounts of the respective salts, and no two boiler waters are alike.

The subject is further complicated by the presence of sodium nitrate, sodium carbonate and caustic soda, and a very complex situation may arise as to the solubility of sulphate of soda in solutions of any or all of these bodies, or, on the other hand, by the solubility of these salts in a solution of sulphate of soda, at temperatures of about 400° F. and 200 lb. pressure and upwards. It must, however, be pointed out, that the soda salts other than the sulphate seldom if ever form any appreciable percentage of the scale, whereas some scales contain as much as $\frac{2}{3}$ of their weight of sulphate of soda. The following is an example:—

Sulphate of Soda Scale

Silica	1.35
Oxide of Iron56
Sulphate of Lime	14.45
Carbonate of Lime	15.30
Magnesia	2.20
Sulphate of Sodium	66.56

100.42

The boiler water from which it was deposited contained 10,950 grains of sulphate of soda, and 2210 grains of chloride of sodium per gallon.

Another example is as follows :—

Silica	69
Sulphate of Lime	43·81
Sulphate of Sodium	52·09
Magnesia	1·32
Water, etc.	2·09
	<hr/>
	100·00
	<hr/>

This scale also contains a large quantity of sulphate of lime, and is really a double sulphate of lime and soda, and may be considered to be artificial glauberite ($\text{CaSO}_4\text{Na}_2\text{SO}_4$). The scale was disintegrated when put into pure water, the sulphate of soda dissolving up and leaving the sulphate of lime as an insoluble powder. Although sulphate of lime possesses the property of forming a double salt with sulphate of soda, this only takes place in concentrated boiler waters, and further illustrates the tendency of sulphate of soda to separate out from concentrated solutions. If the boiler water is not concentrated sulphate of lime comes down without bringing any sulphate of soda with it. As one illustration out of many, the following may be given :—

Boiler Water

Sulphate of Lime	45·65
Sulphate of Magnesia	2·31
Sulphate of Sodium	370·50
Nitrate of Sodium	23·80
Chloride of Sodium	327·60
	<hr/>
	769·86
	<hr/>

Scale

Silica	31
Oxide of Iron	4·70
Sulphate of Lime	87·25
Magnesia	7·73
	<hr/>
	99·99
	<hr/>

These analyses and experiments illustrate the tendency of sulphate of soda to come out of solution when the boiler water becomes somewhat concentrated. What that concentration is,

is not exactly known and no doubt depends upon the amounts of the other soluble constituents of the boiler water, and possibly also upon the rapidity of evaporation. When a solution of soda salts is evaporated on a hot iron plate, the formation of a saline film next the plate is clearly visible long before the water is evaporated off, and when a boiler surface is rapidly evaporating a strong solution of soluble salts, that portion of the water next to the heating surface is bound to become even more concentrated and may become so concentrated as to cover the surface of the iron with a crystalline deposit of these soluble salts, or it may become so concentrated that one or more of the soluble salts becomes insoluble in the solution of the others, the result being the same, viz. the formation of a saline deposit which acts exactly like an insoluble scale or incrustation and causes overheating of the plates or tubes. In many cases where failure of the heating surfaces has taken place without any visible cause, failure has probably been brought about in this way. Many perfectly clean tubes have been known to fail by becoming blistered on the outside without any evidence of internal scale, and as the blistering could only have taken place at a temperature at which sulphate of soda fuses on the outside, there must have been some internal resistance to the passage of heat, to allow the temperature of the tube to rise to 1700°F . So far as can be seen from an examination of the tube and the composition of the boiler water this could only have been brought about by an internal deposition of some soda salt, most probably the sulphate, so that the tubes have been subjected to the action of sulphate of soda both on the inside and the outside. The internal sulphate has acted as a partial insulator, and therefore allowed the external sulphate to melt and so destroy the tube.

As sulphate of soda becomes more soluble as the temperature falls, this saline scale would not be found when the boiler was opened, as it would dissolve up again as the boiler cooled down, and the only evidence it would leave of its temporary presence would be the blister itself.

It is also possible that a boiler water concentrated beyond a certain limit may become less fluid and mobile, and tend to assume a syrupy consistency at the temperature then obtaining in the boiler, or to put it in another way, the concentrated boiler water, or at least that portion of it in immediate or partial contact with the heating surface may tend to become colloidal. Colloidal bodies do not have the same mobility and freedom

of movement as non-colloidal bodies, and would therefore be inclined to linger on the heating surface or even become attached to it. It is well known that colloidal bodies do stick to heated surfaces, and overheating might be brought about either by direct adherence or by the partially adhesive body imprisoning pockets of steam, whereby the transmission of heat would be retarded, and in a hard-worked boiler this retardation might conceivably be sufficient to cause the overheating necessary for the blistering and destruction of the tubes.

It is also known that the yield of distilled water from multiple effect evaporators evaporating sea-water is considerably diminished when the brine used is concentrated beyond a certain degree, and it is further known that where cast-iron vessels are used to concentrate crystallizable liquids, the adherence of any solid or crystalline deposit causes the cast-iron to crack, owing to the lack of transmission of the heat at that particular spot.

Many theories could be advanced to account for this overheating, but it is at least reasonable to suppose that a concentrated solution of sulphate of soda does in some way or other retard the transmission of heat from the metal to the water. Modern boilers are designed to *fully* utilize every square foot of heating surface, and in a case like this, where it is not possible to see into the inside of the boiler under working conditions, any theory, even if apparently remote, which may help to throw light on this retardation of heat, deserves careful consideration, and should not be turned down without patient investigation.

No figures can be given for the concentration of the boiler water, as this would probably be different for every water and largely dependent upon the rate at which the boiler was worked, but as it is known that no evil effects are experienced when the total solids are kept at about 1000 grains per gallon, this would appear to be a safe limit. No doubt this is often exceeded, but it is not good practice to run to a concentration at which there is any danger of the deposition of a saline deposit, especially if the boilers are hard worked.

The fact that sulphate of soda has a remarkable tendency to form supersaturated solutions must also not be overlooked. These supersaturated solutions suddenly solidify under certain conditions, and these conditions may possibly be brought about under the working conditions of a boiler.

WATER SUPPLIES

THE following analyses are typical examples of the supplies they represent. The waters themselves may vary a little from time to time, but the analyses give a fairly accurate idea of the constituents of these waters. The variation will be greatest in the soft waters, which may sometimes be faintly acid, sometimes neutral and sometimes slightly alkaline. This fact should not be overlooked when considering the suitability of a soft water for boiler feed. Soft waters may be dangerous as feed waters, not because they are soft, but because the small amount of dissolved matter may be acid or may develop acid when the water is heated in the boilers.

BRITISH TOWN WATERS

<i>Barrow-in-Furness</i>		<i>Birkenhead</i>	
Silica	•16	Silica	•20
Oxide of Iron	•14	Oxide of Iron	•13
Sulphate of Lime	1•09	Sulphate of Lime	1•58
Sulphate of Magnesia	•19	Carbonate of Lime	10•23
Formate of Magnesia	•65	Sulphate of Magnesia	4•72
Chloride of Sodium	•41	Nitrate of Magnesia	2•59
	<hr/>	Chloride of Magnesia	9•00
	2•64		<hr/>
	<hr/>		28•45
Hardness	1•50°	Hardness	17•20°
<i>Bedford</i>		<i>Boston (Lincolns.)</i>	
Silica	•19	Silica	•19
Oxide of Iron	•15	Oxide of Iron	•13
Sulphate of Lime	4•92	Sulphate of Lime	3•22
Carbonate of Lime	17•50	Carbonate of Lime	8•54
Sulphate of Magnesia	3•78	Sulphate of Magnesia	•63
Sulphate of Sodium	3•40	Chloride of Sodium	3•28
Chloride of Sodium	4•10		<hr/>
	<hr/>		15•99
	34•04		<hr/>
Hardness	24•25°	Hardness	11•43°
<i>Belfast</i>		<i>Bradford</i>	
Silica	•17	Silica	•10
Oxide of Iron	•17	Oxide of Iron	•07
Sulphate of Lime	1•19	Sulphate of Lime	2•28
Carbonate of Lime	1•82	Carbonate of Lime	2•45
Sulphate of Magnesia	•39	Sulphate of Magnesia	1•50
Chloride of Magnesia	1•27	Chloride of Sodium	1•47
Chloride of Sodium	•90		<hr/>
	<hr/>		7•87
	5•91		<hr/>
Hardness	4•38°	Hardness	5•40°

Bristol

Silica	19
Oxide of Iron	12
Carbonate of Lime	12.89
Carbonate of Magnesia	46
Sulphate of Magnesia	84
Nitrate of Sodium	89
Sulphate of Sodium	1.90
Chloride of Sodium	2.87

20.16

Hardness 14.14°
Chatham

Silica	20
Oxide of Iron	13
Sulphate of Lime	1.05
Carbonate of Lime	16.09
Nitrate of Lime	1.23
Sulphate of Magnesia	1.14
Nitrate of Sodium	1.10
Chloride of Sodium	9.00

29.94

Hardness 18.55°
Chester

Silica	20
Oxide of Iron	08
Sulphate of Lime	1.43
Carbonate of Lime	5.95
Sulphate of Magnesia	1.36
Chloride of Magnesia78
Chloride of Sodium	1.48

11.28

Hardness 8.96°
Coventry

Silica	19
Oxide of Iron	11
Sulphate of Lime	2.50
Carbonate of Lime	11.90
Sulphate of Magnesia	6.12
Nitrate of Sodium	2.09
Chloride of Sodium	2.45

25.36

Hardness 18.85°
Darlington

Silica	36
Oxide of Iron	14
Sulphate of Lime	1.41
Carbonate of Lime	2.78
Chloride of Magnesia40
Crenate of Magnesia	1.38
Chloride of Sodium	1.15
Peaty Matters	1.43

9.05

Hardness 4.95°
Derby

Silica	20
Oxide of Iron	14
Sulphate of Lime	3.25
Carbonate of Lime	14.00
Sulphate of Magnesia	5.58
Nitrate of Sodium	1.48
Sulphate of Sodium62
Chloride of Sodium	2.46

27.73

Hardness 21.05°
Doncaster

Silica	16
Oxide of Iron	11
Sulphate of Lime	2.45
Sulphate of Magnesia	1.15
Formate of Magnesia	1.67
Chloride of Sodium	1.63
Formic Acid26

6.43

Hardness 3.40°

This sample is acid.

Falmouth

Silica	20
Oxide of Iron	12
Carbonate of Lime	1.40
Carbonate of Magnesia23
Sulphate of Magnesia	1.92
Nitrate of Sodium	2.97
Sulphate of Sodium	2.90
Chloride of Sodium	4.50

14.24

Hardness 3.30°

Frome

Silica	·18
Oxide of Iron	·11
Carbonate of Lime	17·69
Carbonate of Magnesia	1·60
Sulphate of Magnesia	·72
Nitrate of Sodium	1·48
Sulphate of Sodium	1·15
Chloride of Sodium	2·87
	<u>25·80</u>
Hardness	20·19°

Gt. Yarmouth

Silica	·20
Oxide of Iron	·11
Sulphate of Lime	6·00
Carbonate of Lime	11·20
Sulphate of Magnesia	2·02
Chloride of Magnesia	·65
Nitrate of Sodium	·29
Chloride of Sodium	9·16
	<u>29·63</u>
Hardness	17·95°

Grimsby

Silica	·17
Oxide of Iron	·07
Carbonate of Lime	15·20
Carbonate of Magnesia	·97
Sulphate of Magnesia	1·20
Nitrate of Sodium	1·19
Sulphate of Sodium	·57
Chloride of Sodium	5·73
	<u>25·10</u>
Hardness	17·35°

Guernsey

Silica	·18
Oxide of Iron	·10
Sulphate of Lime	·73
Carbonate of Lime	3·54
Chloride of Magnesia	·95
Nitrate of Sodium	3·57
Chloride of Sodium	11·12
Sulphate of Magnesia	3·64
	<u>23·83</u>
Hardness	8·00°

Hanley

Silica	·20
Oxide of Iron	·14
Carbonate of Lime	8·11
Carbonate of Magnesia	·47
Sulphate of Magnesia	1·47
Nitrate of Magnesia	2·95
Chloride of Sodium	1·64
	<u>14·98</u>
Hardness	11·80°

Hartlepool

Silica	·22
Oxide of Iron	·17
Sulphate of Lime	4·39
Carbonate of Lime	20·55
Sulphate of Magnesia	18·49
Nitrate of Sodium	1·12
Chloride of Sodium	18·02
	<u>62·96</u>
Hardness	39·18°

Hull

Silica	·13
Oxide of Iron	·06
Sulphate of Lime	1·72
Carbonate of Lime	13·21
Nitrate of Lime	1·58
Carbonate of Magnesia	·90
Chloride of Sodium	2·86
	<u>20·46</u>
Hardness	16·53°

Ipswich

Silica	·20
Oxide of Iron	·08
Sulphate of Lime	3·16
Carbonate of Lime	20·29
Sulphate of Magnesia	·36
Nitrate of Magnesia	2·44
Nitrate of Sodium	·80
Chloride of Sodium	5·32
	<u>32·65</u>
Hardness	24·55°

Kettering

Silica	·19
Oxide of Iron	·21
Sulphate of Lime	1·52
Carbonate of Lime	11·90
Sulphate of Magnesia	2·52
Sulphate of Sodium	1·10
Chloride of Sodium	2·86

20·30

Hardness 15·10°
Lancaster

Silica	·18
Oxide of Iron	·11
Carbonate of Lime	·30
Sulphate of Magnesia	·60
Chloride of Sodium	1·64

2·83

Hardness ·80°
Limerick

Silica	·10
Oxide of Iron	·05
Sulphate of Lime	10·70
Carbonate of Lime	4·90
Sulphate of Magnesia	2·64
Chloride of Sodium	2·45

20·84

Hardness 14·95°
Llanelly

Silica	·18
Oxide of Iron	·13
Sulphate of Lime	1·24
Carbonate of Lime	·41
Chloride of Calcium	·86
Chloride of Magnesia	1·06
Chloride of Sodium	1·07

4·95

Hardness 3·20°
Loughborough

Silica	·22
Oxide of Iron	·08
Sulphate of Lime	2·08
Carbonate of Lime	5·95
Sulphate of Magnesia	3·04
Nitrate of Magnesia	3·73
Chloride of Sodium	2·05

17·15

Hardness 12·55°
Luton

Silica	·17
Oxide of Iron	·08
Sulphate of Lime	2·07
Carbonate of Lime	14·35
Nitrate of Lime	3·89
Sulphate of Magnesia	·87
Nitrate of Sodium	·70
Chloride of Sodium	2·87

25·00

Hardness 15·97°
Macclesfield

Silica	·14
Oxide of Iron	·11
Sulphate of Lime	1·62
Carbonate of Lime	2·80
Sulphate of Magnesia	2·10
Chloride of Sodium	1·63

8·40

Hardness 5·75°
Newcastle

Silica	·17
Oxide of Iron	·15
Sulphate of Lime	1·10
Carbonate of Lime	6·02
Sulphate of Magnesia	1·35
Formate of Magnesia	3·45
Chloride of Sodium	2·05
Peaty Matters	1·20

15·49

Hardness 10·95°
Northampton

Silica	·18
Oxide of Iron	·10
Sulphate of Lime	·63
Carbonate of Lime	7·84
Sulphate of Magnesia	1·50
Nitrate of Sodium	1·48
Sulphate of Sodium	·71
Chloride of Sodium	3·28

15·72

Hardness 9·55°

<i>Oldham</i>	
Silica	·23
Oxide of Iron	·10
Sulphate of Lime	2·99
Sulphate of Magnesia	1·41
Nitrate of Sodium	·59
Chloride of Sodium	2·05
	<u>7·37</u>
Hardness	3·38°

<i>Portsmouth</i>	
Silica	·18
Oxide of Iron	·10
Carbonate of Lime	15·68
Nitrate of Lime	·21
Sulphate of Magnesia	·75
Nitrate of Magnesia	·33
Nitrate of Sodium	1·18
Chloride of Sodium	3·28
	<u>21·71</u>
Hardness	16·65°

<i>Ripon</i>	
Silica	·28
Oxide of Iron	·17
Sulphate of Lime	·94
Carbonate of Lime	1·75
Sulphate of Magnesia	1·44
Chloride of Sodium	1·22
	<u>5·80</u>
Hardness	3·65°

<i>Rugby</i>	
Silica	·28
Oxide of Iron	·11
Sulphate of Lime	2·87
Carbonate of Lime	17·50
Sulphate of Magnesia	4·68
Nitrate of Sodium	1·49
Chloride of Sodium	3·28
	<u>30·21</u>
Hardness	23·50°

<i>Runcorn</i>	
Silica	·16
Oxide of Iron	·10
Sulphate of Lime	·56
Chloride of Calcium	·43
Chloride of Magnesium	·48
Chloride of Sodium	1·42
Peaty Matter	·38
	<u>3·53</u>
Hardness	1·30°

<i>Sheffield</i>	
Silica	·24
Oxide of Iron	·09
Sulphate of Lime	·50
Carbonate of Lime	1·95
Sulphate of Magnesia	1·26
Sulphate of Sodium	·32
Chloride of Sodium	1·97
	<u>6·33</u>
Hardness	3·35°

<i>Shipley</i>	
Silica	·20
Oxide of Iron	·11
Sulphate of Lime	2·99
Chloride of Magnesia	·79
Chloride of Sodium	1·48
	<u>5·57</u>
Hardness	3·03°

<i>Shrewsbury</i>	
Silica	·27
Oxide of Iron	·16
Carbonate of Lime	13·00
Carbonate of Magnesia	3·19
Sulphate of Magnesia	2·94
Nitrate of Sodium	2·38
Chloride of Sodium	3·69
	<u>25·63</u>
Hardness	19·25°

South Shields

Silica	·28
Oxide of Iron	·10
Carbonate of Lime	14·70
Carbonate of Magnesia	3·40
Sulphate of Magnesia	5·31
Nitrate of Magnesia	4·40
Chloride of Magnesia	·31
Chloride of Sodium	6·60

 35·10

Hardness 26·48°

St. Helens

Silica	·17
Oxide of Iron	·09
Carbonate of Lime	4·20
Carbonate of Magnesia	5·06
Sulphate of Magnesia	2·88
Sulphate of Sodium	1·97
Chloride of Sodium	4·91

 19·28

Hardness 12·60°

Southampton

Silica	·18
Oxide of Iron	·14
Carbonate of Lime	10·30
Sulphate of Magnesia	1·06
Nitrate of Magnesia	·41
Nitrate of Sodium	1·30
Chloride of Sodium	2·05

 15·44

Hardness 11·45°

Southport

Silica	·22
Oxide of Iron	·11
Carbonate of Lime	9·50
Carbonate of Magnesia	5·07
Sulphate of Magnesia	1·20
Nitrate of Sodium	1·19
Sulphate of Sodium	1·60
Chloride of Sodium	4·10

 22·99

Hardness 16·50°

Q

Stockport

Silica	·11
Oxide of Iron	·08
Sulphate of Lime	1·21
Carbonate of Lime	2·98
Sulphate of Magnesia	2·04
Sulphate of Sodium	5·27
Chloride of Sodium	2·46

 14·15

Hardness 5·58°

Stoke-on-Trent

Silica	·20
Oxide of Iron	·15
Carbonate of Lime	7·89
Carbonate of Magnesia	1·96
Sulphate of Magnesia	1·35
Nitrate of Sodium	2·38
Sulphate of Sodium	·35
Chloride of Sodium	3·28

 17·56

Hardness 11·34°

Sunderland

Silica	·18
Oxide of Iron	·09
Carbonate of Lime	14·20
Carbonate of Magnesia	4·87
Sulphate of Magnesia	5·19
Nitrate of Magnesia	2·07
Chloride of Magnesia	1·03
Chloride of Sodium	4·88

 32·51

Hardness 32·51°

Swindon

Silica	·19
Oxide of Iron	·13
Sulphate of Lime	·29
Carbonate of Lime	21·28
Sulphate of Magnesia	1·20
Sulphate of Sodium	1·24
Chloride of Sodium	2·87

 27·20

Hardness 22·50°

<i>Tamworth</i>	
Silica	·28
Oxide of Iron	·06
Sulphate of Lime	5·49
Carbonate of Lime	10·85
Sulphate of Magnesia	1·52
Nitrate of Sodium	3·41
Sulphate of Sodium	·49
Chloride of Sodium	4·10
	<hr/>
	26·20
	<hr/>
Hardness	16·25°

<i>Warrington</i>	
Silica	·18
Oxide of Iron	·07
Carbonate of Lime	10·80
Carbonate of Magnesia	·93
Sulphate of Magnesia	4·59
Nitrate of Magnesia	3·00
Chloride of Sodium	2·47
	<hr/>
	22·04
	<hr/>
Hardness	17·75°

<i>Whitehaven</i>	
Silica	·18
Oxide of Iron	·12
Sulphate of Lime	·51
Carbonate of Lime	·21
Carbonate of Magnesia	·50
Nitrate of Sodium	·13
Chloride of Sodium	2·46
	<hr/>
	4·11
	<hr/>
Hardness	1·19°

<i>Wigan</i>	
Silica	·18
Oxide of Iron	·10
Sulphate of Lime	4·15
Carbonate of Lime	2·79
Nitrate of Lime	·58
Sulphate of Magnesia	2·37
Chloride of Magnesia	1·37
Chloride of Sodium	·77
	<hr/>
	12·3
	<hr/>
Hardness	9·35°

<i>Wolverhampton</i>	
Silica	·18
Oxide of Iron	·12
Carbonate of Lime	11·20
Carbonate of Magnesia	·59
Sulphate of Magnesia	4·02
Nitrate of Sodium	2·08
Sulphate of Sodium	1·90
Chloride of Sodium	4·50
	<hr/>
	24·59
	<hr/>
Hardness	15·25°

<i>Workington</i>	
Silica	·17
Oxide of Iron	·12
Carbonate of Lime	·50
Carbonate of Magnesia	·29
Sulphate of Sodium	·42
Carbonate of Sodium	·53
Chloride of Sodium	2·05
	<hr/>
	4·08
	<hr/>
Hardness	·85°

EUROPEAN WATERS

<i>Barcelona</i>	
Silica	·20
Oxide of Iron	·08
Carbonate of Lime	12·71
Carbonate of Magnesia	1·78
Sulphate of Magnesia	3·87
Nitrate of Sodium	1·78
Chloride of Sodium	9·42
	<hr/>
	29·84
	<hr/>
Hardness	18·05°

<i>Brussels</i>	
Silica	·28
Oxide of Iron	·73
Sulphate of Lime	·27
Carbonate of Lime	3·50
Sulphate of Magnesia	1·08
Sulphate of Sodium	10·95
Chloride of Sodium	10·24
	<hr/>
	27·05
	<hr/>
Hardness	4·60°

Brussels (Canal)

Silica	28
Oxide of Iron	14
Carbonate of Lime	17.01
Sulphate of Magnesia	5.10
Sulphate of Sodium	3.76
Chloride of Sodium	4.09

30.38

Hardness 21.26°
Constantinople

Silica	48
Oxide of Iron	13
Carbonate of Lime	21.60
Carbonate of Magnesia	1.34
Sulphate of Sodium	44
Carbonate of Sodium	1.40
Chloride of Sodium	2.87

28.26

Hardness 23.20°
Copenhagen

Silica	12
Oxide of Iron	16
Carbonate of Lime	75
Carbonate of Magnesia	46
Sulphate of Sodium	2.10
Chloride of Sodium	1.64
Carbonate of Sodium	17

5.40

Hardness 1.30°
Ostend

Silica	1.22
Oxide of Iron	16
Sulphate of Lime	5.44
Carbonate of Lime	2.10
Sulphate of Magnesia	2.58
Nitrate of Sodium	1.48
Sulphate of Sodium	30
Chloride of Sodium	4.91

18.19

Hardness 8.25°
Paris

Silica	30
Oxide of Iron	21
Sulphate of Lime	2.21
Carbonate of Lime	17.23
Sulphate of Magnesia	5.61
Chloride of Sodium	2.05

27.61

Hardness 23.56°
Paris (R. Seine)

Silica	21
Oxide of Iron	10
Carbonate of Lime	15.14
Sulphate of Magnesia	1.68
Nitrate of Sodium	1.49
Sulphate of Sodium	75
Chloride of Sodium	1.64

21.01

Hardness 16.54°
Petrograd

Silica	08
Oxide of Iron	09
Sulphate of Lime	92
Carbonate of Lime	72
Nitrate of Lime	1.00
Carbonate of Magnesia	92
Chloride of Sodium	3.67

7.40

Hardness 3.10°
Petrograd (Canal)

Silica	24
Oxide of Iron	14
Crenate of Lime	8.42
Nitrate of Lime	1.15
Sulphate of Magnesia	54
Chloride of Magnesia	68
Chloride of Sodium	2.80

13.97

Hardness 3.15°

<i>Rotterdam</i>	
Silica	·24
Alumina	2·69
Sulphate of Lime	3·96
Carbonate of Lime	4·20
Nitrate of Lime	1·15
Sulphate of Magnesia	·54
Chloride of Sodium	5·32
	<u>18·10</u>
Hardness	8·25°

<i>Seville</i>	
Silica	·18
Oxide of Iron	·12
Carbonate of Lime	13·50
Sulphate of Magnesia	·90
Nitrate of Magnesia	·74
Nitrate of Sodium	2·54
Chloride of Sodium	4·10
	<u>22·08</u>
Hardness	14·75°

<i>Teneriffe</i>	
Silica	·11
Oxide of Iron	·06
Carbonate of Lime	3·11
Carbonate of Magnesia	1·99
Nitrate of Sodium	·59
Sulphate of Sodium	1·10
Chloride of Sodium	5·32
	<u>12·28</u>
Hardness	5·49°

<i>Valencia</i>	
Silica	·15
Oxide of Iron	·05
Sulphate of Lime	·45
Carbonate of Lime	2·80
Sulphate of Magnesia	1·26
Sulphate of Sodium	1·12
Chloride of Sodium	1·64
	<u>7·47</u>
Hardness	4·15°

VARIOUS

<i>Baku</i>	
Silica	·01
Oxide of Iron	·01
Carbonate of Lime	1·00
Carbonate of Magnesia	·34
Nitrate of Sodium	·27
Sulphate of Sodium	1·54
Chloride of Sodium	1·23
	<u>4·40</u>
Hardness	1·40°

<i>Christmas Island</i>	
Silica	·24
Oxide of Iron	·10
Carbonate of Lime	17·39
Carbonate of Magnesia	1·85
Nitrate of Sodium	·89
Sulphate of Sodium	·90
Chloride of Sodium	6·14
	<u>27·51</u>
Hardness	19·59°

<i>Falkland Islands</i>	
Silica	·10
Oxide of Iron	·08
Sulphate of Lime	·68
Chloride of Magnesia	·95
Chloride of Sodium	4·98
Organic Matter	2·80
Free Hydrochloric Acid	·40
	<u>9·99</u>
Hardness	1·50°

<i>Pekin (Canal)</i>	
Silica	·59
Oxide of Iron	·18
Carbonate of Lime	8·40
Carbonate of Magnesia	5·29
Sulphate of Sodium	1·97
Chloride of Sodium	2·45
	<u>18·88</u>
Hardness	14·70°

Rejang (Borneo)

Silica	·16
Oxide of Iron	·12
Carbonate of Lime	·75
Carbonate of Magnesia	·74
Chloride of Sodium	12·28
	<hr/>
	14·05
	<hr/>
Hardness	1·63°

NEW ZEALAND

Auckland (Well)

Silica	·18
Alumina	·22
Carbonate of Lime	2·50
Carbonate of Magnesia	2·03
Sulphate of Magnesia	·75
Nitrate of Magnesia	·59
Nitrate of Sodium	3·80
Chloride of Sodium	2·87
	<hr/>
	12·94
	<hr/>
Hardness	5·95°

SMYRNA (River)

Silica	·18
Oxide of Iron	·13
Carbonate of Lime	13·11
Carbonate of Magnesia	4·40
Sulphate of Magnesia	1·14
Sulphate of Sodium	·54
Chloride of Sodium	2·46
	<hr/>
	21·96
	<hr/>
Hardness	19·31°

SOUTH AMERICA

Bahia

Silica	·39
Oxide of Iron	·17
Carbonate of Lime	5·05
Sulphate of Magnesia	2·10
Nitrate of Sodium	1·20
Sulphate of Sodium	1·24
Chloride of Sodium	4·91
	<hr/>
	15·06
	<hr/>
Hardness	6·80°

Buenos Ayres

Silica	·30
Alumina	·24
Carbonate of Lime	6·71
Carbonate of Magnesia	1·41
Sulphate of Magnesia	·33
Sulphate of Sodium	·85
Chloride of Sodium	2·05
	<hr/>
	11·89
	<hr/>
Hardness	8·66°

Para River

Silica	5·32
Alumina	1·96
Carbonate of Lime	·80
Carbonate of Magnesia	·46
Sulphate of Sodium	·90
Chloride of Sodium	2·05
	<hr/>
	11·49
	<hr/>
Hardness	1·35°

River Plate

Silica	2·69
Alumina	·50
Carbonate of Lime	3·50
Carbonate of Magnesia	·93
Sulphate of Magnesia	1·02
Nitrate of Sodium	·59
Sulphate of Sodium	1·88
Chloride of Sodium	8·60
	<hr/>
	19·71
	<hr/>
Hardness	5·45°

Rosario (R. Parana)

Silica	5·32
Alumina	1·34
Carbonate of Lime	2·11
Sulphate of Magnesia	1·62
Sulphate of Sodium	1·42
Chloride of Sodium	5·32
	<hr/>
	17·13
	<hr/>
Hardness	3·46°

BRAZIL (*Wells at Railway Stations*)

(1)	
Silica	·26
Oxide of Iron	·18
Carbonate of Lime	3·43
Sulphate of Magnesia	·45
Nitrate of Magnesia	2·59
Chloride of Sodium	8·60
	<hr/>
	15·51
	<hr/>
Hardness	5·52°

(2)	
Silica	·25
Oxide of Iron	·20
Carbonate of Lime	4·89
Carbonate of Magnesia	·72
Sulphate of Magnesia	2·88
Chloride of Magnesia	1·73
Chloride of Sodium	20·00
	<hr/>
	30·67
	<hr/>
Hardness	9·95°

Pernambuco (Town)

Silica	·28
Alumina	·35
Sulphate of Lime	·80
Carbonate of Lime	1·06
Nitrate of Lime	1·06
Chloride of Magnesia	·64
Chloride of Sodium	1·66
	<hr/>
	5·85
	<hr/>
Hardness	2·67°

CHILE (*Valparaiso*)

Silica	·36
Oxide of Iron	·10
Carbonate of Lime	2·50
Carbonate of Magnesia	1·76
Sulphate of Sodium	·25
Carbonate of Sodium	2·12
Chloride of Sodium	·84
	<hr/>
	7·93
	<hr/>
Hardness	4·60°

ECUADOR (*R. Daule*)

Silica	3·44
Alumina	·84
Carbonate of Lime	2·00
Carbonate of Magnesia	·88
Nitrate of Sodium	·15
Sulphate of Sodium	1·12
Chloride of Sodium	1·22
	<hr/>
	9·65
	<hr/>
Hardness	3·05°

PERU (*Callao*)

Silica	·27
Alumina	·17
Sulphate of Lime	2·72
Carbonate of Lime	7·70
Sulphate of Magnesia	1·77
Sulphate of Sodium	2·80
Chloride of Sodium	3·69
	<hr/>
	19·12
	<hr/>
Hardness	11·18°

Peru (R. Chira)

Silica	7·28
Alumina	·14
Carbonate of Lime	5·00
Carbonate of Magnesia	1·62
Sulphate of Sodium	3·07
Carbonate of Sodium	1·38
Chloride of Sodium	1·22
	<hr/>
	19·71
	<hr/>
Hardness	6·92°

Lima (Peru)

Silica	·23
Oxide of Iron	·15
Carbonate of Lime	12·39
Sulphate of Magnesia	3·27
Sulphate of Sodium	3·23
Chloride of Sodium	4·10
	<hr/>
	23·37
	<hr/>
Hardness	15·18°

MEXICO

River Sabinas

Silica	·90
Oxide of Iron	·24
Sulphate of Lime	5·03
Carbonate of Lime	11·20
Sulphate of Magnesia	4·80
Sulphate of Sodium	6·81
Chloride of Sodium	5·73

34·71

Hardness 18·90°

Tancoil (Well)

Silica	·26
Oxide of Iron	·25
Sulphate of Lime	14·86
Carbonate of Lime	10·07
Sulphate of Magnesia	10·86
Sulphate of Sodium	1·38
Chloride of Sodium	4·10

41·78

Hardness 30·05°

Tucuman (Well)

Silica	2·69
Alumina	·18
Carbonate of Lime	15·11
Carbonate of Magnesia	2·23
Sulphate of Sodium	10·76
Carbonate of Sodium	5·18
Chloride of Sodium	4·10

40·25

Hardness 17·76°

WEST INDIES

Antigua

Silica	·62
Oxide of Iron	·37
Sulphate of Lime	1·39
Carbonate of Lime	1·48
Chloride of Magnesia	1·63
Chloride of Sodium	1·70

7·19

Hardness 4·22°

CUBA

Belmez (Town)

Silica	1·10
Oxide of Iron	·08
Carbonate of Lime	7·50
Carbonate of Magnesia	6·09
Nitrate of Sodium	1·78
Sulphate of Sodium	1·06
Carbonate of Sodium	·70
Chloride of Sodium	2·46

20·77

Hardness 14·75°

Candalaria (Well)

Silica	·65
Oxide of Iron	·09
Carbonate of Lime	9·30
Carbonate of Magnesia	3·28
Sulphate of Sodium	2·55
Carbonate of Sodium	5·59
Chloride of Sodium	14·73

35·79

Hardness 13·20°

Cruces (Well)

Silica	·21
Oxide of Iron	·16
Carbonate of Lime	26·62
Nitrate of Lime	2·43
Sulphate of Magnesia	8·04
Nitrate of Magnesia	18·52
Chloride of Magnesia	4·94
Chloride of Sodium	24·60

85·52

Hardness 52·15°

Demerara (Sugar Estate)

Silica	1·12
Alumina, etc.	·45
Carbonate of Lime	9·30
Carbonate of Magnesia	9·62
Sulphate of Sodium	6·77
Carbonate of Sodium	12·17
Chloride of Sodium	18·43
Organic Matter	6·96

64·82

Hardness 20·75°

St. Kitts

Silica	3.02
Alumina10
Carbonate of Lime	1.50
Sulphate of Magnesia75
Chloride of Magnesia74
Chloride of Sodium	1.94
	<hr/>
	8.05
	<hr/>
Hardness	2.90°

BURMA

Kamoh

Silica22
Oxide of Iron15
Sulphate of Lime	2.31
Carbonate of Lime	6.50
Carbonate of Magnesia	12.18
Chloride of Magnesia	1.22
	<hr/>
	22.58
	<hr/>
Hardness	22.70°

Manpur

Silica84
Oxide of Iron12
Carbonate of Lime	7.80
Carbonate of Magnesia	4.18
Sulphate of Magnesia57
Chloride of Sodium80
	<hr/>
	14.31
	<hr/>
Hardness	13.25°

Topah

Silica21
Oxide of Iron14
Sulphate of Lime54
Sulphate of Magnesia60
Chloride of Sodium82
Free Acid27
	<hr/>
	2.58
	<hr/>
Hardness90°

The acid was calculated as H_2SO_4 .

JAPAN

Amagasaki

Silica18
Alumina75
Carbonate of Lime	2.50
Carbonate of Magnesia	2.98
Sulphate of Sodium	1.70
Carbonate of Sodium	1.90
Chloride of Sodium	16.38
	<hr/>
	26.39
	<hr/>

Hardness 6.05°

Kobe

Silica17
Alumina	2.10
Sulphate of Lime	9.06
Carbonate of Lime	5.89
Chloride of Calcium	22.36
Chloride of Magnesia	14.41
	<hr/>
	53.99
	<hr/>

Hardness 48.05°

Muigi

Silica39
Oxide of Iron16
Carbonate of Lime	3.11
Carbonate of Magnesia63
Carbonate of Sodium	1.11
Chloride of Sodium	4.91
	<hr/>
	10.31
	<hr/>
Hardness	3.86°

Yokohama

Silica	1.28
Oxide of Iron23
Carbonate of Lime	3.10
Carbonate of Magnesia	1.64
Sulphate of Magnesia	1.32
Sulphate of Sodium	5.47
Chloride of Sodium	2.47
	<hr/>
	15.51
	<hr/>

Hardness 7.30°

INDIA

Bombay

Silica	19
Oxide of Iron	12
Carbonate of Lime	189
Carbonate of Magnesia	101
Sulphate of Sodium	43
Carbonate of Sodium	46
Chloride of Sodium	163

5.73

Hardness 3.09°

Calcutta

Silica	27
Oxide of Iron	13
Carbonate of Lime	865
Sulphate of Magnesia	123
Chloride of Magnesia	156
Chloride of Sodium	833

20.17

Hardness 11.30°

River Hoogley

Silica	37
Alumina	190
Carbonate of Lime	499
Carbonate of Magnesia	222
Sulphate of Sodium	170
Carbonate of Sodium	159
Chloride of Sodium	205

14.82

Hardness 6.44°

Delhi

Silica	24
Oxide of Iron	20
Carbonate of Lime	1022
Sulphate of Magnesia	628
Chloride of Magnesia	74
Nitrate of Sodium	178
Chloride of Sodium	1638

35.84

Hardness 16.22°

Jubbulpore (Municipal Reservoir)

Silica	19
Alumina	14
Carbonate of Lime	350
Carbonate of Magnesia	155
Sulphate of Sodium	22
Carbonate of Sodium	27
Chloride of Sodium	123

7.10

Hardness 5.35°

Bhopal Lake

Silica	31
Alumina	13
Carbonate of Lime	210
Carbonate of Magnesia	139
Sulphate of Sodium	21
Carbonate of Sodium	188
Chloride of Sodium	124

7.26

Hardness 3.75°

River Agra

Silica	28
Alumina	13
Carbonate of Lime	539
Carbonate of Magnesia	483
Nitrate of Sodium	148
Sulphate of Sodium	699
Carbonate of Sodium	82
Chloride of Sodium	773

27.65

Hardness 11.14°

River Valdona

Silica	18
Alumina	13
Carbonate of Lime	319
Carbonate of Magnesia	265
Sulphate of Sodium	23
Carbonate of Sodium	70
Chloride of Sodium	164

8.72

Hardness 6.34°

<i>Gwalior (Well)</i>	
Silica	·87
Alumina	·12
Carbonate of Lime	7·89
Carbonate of Magnesia	9·20
Nitrate of Sodium	2·08
Sulphate of Sodium	1·56
Carbonate of Sodium	13·70
Chloride of Sodium	3·68
	<hr/>
	39·10
	<hr/>
Hardness	18·84°

<i>Poona (Well)</i>	
Silica	·20
Alumina	·16
Carbonate of Lime	4·98
Carbonate of Magnesia	5·84
Sulphate of Sodium	·50
Carbonate of Sodium	4·43
Chloride of Sodium	4·10
	<hr/>
	20·21
	<hr/>
Hardness	11·93°

APPENDIX

CARBONIC ACID

FREE and Fixed Carbonic Acid in Kent Co.'s Water daily, from April 21, 1904, to April 30, 1905, being the figures on which the diagrams on pp. 19-24 have been constructed. The figures are in grains per gallon.

<i>Date.</i>	<i>Combined Car- bonic Acid.</i>	<i>Free Car- bonic Acid.</i>	<i>Date.</i>	<i>Combined Car- bonic Acid.</i>	<i>Free Car- bonic Acid.</i>
April 21	. 7.39	10.78	May 29	. 7.21	9.39
22	. 7.25	10.01	30	. 7.21	9.70
23	. 7.21	10.78	31	. 7.27	9.24
24	. 7.15	9.55	June 1	. 7.33	10.78
25	. 7.15	9.09	2	. 7.33	9.16
26	. 7.21	9.70	3	. 7.15	8.93
27	. 7.21	9.24	4	. 7.15	9.39
28	. 7.21	9.47	5	. 7.45	8.93
29	. 7.21	9.70	6	. 7.39	9.39
30	. 7.27	6.32	7	. 7.27	9.86
May 1	. 7.33	9.40	8	. 7.57	9.16
2	. 7.21	9.86	9	. 7.57	11.70
3	. 7.15	9.70	10	. 7.27	10.93
4	. 7.21	10.32	11	. 7.27	7.31
5	. 7.27	10.32	12	. 7.52	8.47
6	. 7.39	10.78	13	. 7.21	10.78
7	. 7.36	9.70	14	. 7.27	9.09
8	. 7.21	9.70	15	. 7.27	9.55
9	. 7.21	9.86	16	. 7.57	10.47
10	. 7.27	9.93	17	. 7.52	9.08
11	. 7.27	9.93	18	. 7.52	8.86
12	. 7.27	10.32	19	. 7.57	8.62
13	. 7.33	11.40	20	. 7.57	10.01
14	. 7.21	11.70	21	. 7.63	8.62
15	. 7.33	8.93	22	. 7.63	9.09
16	. 7.27	9.62	23	. 7.57	9.55
17	. 7.45	10.32	24	. 7.63	10.01
18	. 7.57	10.74	25	. 7.63	9.09
19	. 7.39	9.66	26	. 7.39	10.01
20	. 7.57	10.78	27	. 7.27	8.16
21	. 7.27	9.86	28	. 7.33	9.55
22	. 7.21	9.86	29	. 7.52	9.55
23	. 7.21	8.47	30	. 7.57	10.24
24	. 7.33	8.93	July 1	. 7.57	9.55
25	. 7.21	8.70	2	. 7.39	9.09
26	. 7.27	9.39	3	. 7.33	8.62
27	. 7.27	9.39	4	. 7.33	9.55
28	. 7.33	7.85	5	. 7.45	11.40

Date.	Combined Car- bonic Acid.	Free Car- bonic Acid.	Date.	Combined Car- bonic Acid.	Free Car- bonic Acid.
July 6	. 7.39	10.01	Sept. 3	. 7.45	10.47
7	. 7.63	9.09	4	. 7.52	7.93
8	. 7.39	10.01	5	. 7.45	8.62
9	. 7.45	9.86	6	. 7.45	10.01
10	. 7.57	9.86	7	. 7.52	7.70
11	. 7.39	8.47	8	. 7.52	9.09
12	. 7.57	9.39	9	. 7.39	8.16
13	. 7.57	9.86	10	. 7.33	8.62
14	. 7.45	8.93	11	. 7.45	8.16
15	. 7.52	9.39	12	. 7.33	8.16
16	. 7.52	8.47	13	. 7.45	7.93
17	. 7.57	8.93	14	. 7.39	7.70
18	. 7.45	10.09	15	. 7.39	7.70
19	. 7.52	9.39	16	. 7.45	8.16
20	. 7.52	8.93	17	. 7.33	8.16
21	. 7.52	8.47	18	. 7.27	7.93
22	. 7.57	9.86	19	. 7.39	7.70
23	. 7.39	9.86	20	. 7.33	9.09
24	. 7.45	9.86	21	. 7.27	9.09
25	. 7.33	9.39	22	. 7.39	8.62
26	. 7.21	10.32	23	. 7.33	8.62
27	. 7.33	9.86	24	. 7.39	8.20
28	. 7.33	8.93	25	. 7.33	8.20
29	. 7.33	11.24	26	. 7.33	8.62
30	. 7.39	8.62	27	. 7.39	9.09
31	. 7.39	9.09	28	. 7.33	9.09
Aug. 1	. 7.27	9.55	29	. 7.33	8.62
2	. 7.27	10.01	30	. 7.45	9.09
3	. 7.45	9.55	Oct. 1	. 7.39	9.55
4	. 7.63	10.47	2	. 7.27	7.70
5	. 7.57	9.55	3	. 7.27	8.20
6	. 7.39	9.09	4	. 7.27	8.39
7	. 7.52	9.55	5	. 7.39	8.93
8	. 7.45	9.09	6	. 7.39	7.55
9	. 7.57	9.09	7	. 7.45	7.70
10	. 7.57	10.47	8	. 7.39	7.55
11	. 7.63	10.01	9	. 7.39	7.55
12	. 7.39	9.09	10	. 7.39	7.55
13	. 7.39	10.47	11	. 7.39	7.70
14	. 7.57	8.62	12	. 7.39	7.70
15	. 7.33	9.09	13	. 7.45	8.01
16	. 7.52	8.62	14	. 7.39	8.86
17	. 7.33	9.55	15	. 7.33	8.86
18	. 7.45	10.01	16	. 7.39	7.55
19	. 7.45	8.62	17	. 7.39	8.86
20	. 7.52	9.55	18	. 7.39	7.55
21	. 7.45	9.55	19	. 7.39	7.55
22	. 7.52	9.09	20	. 7.39	8.47
23	. 7.52	8.16	21	. 7.45	8.47
24	. 7.33	9.09	22	. 7.33	8.55
25	. 7.39	9.55	23	. 7.39	9.24
26	. 7.33	10.47	24	. 7.27	9.47
27	. 7.45	10.01	25	. 7.39	7.85
28	. 7.63	9.55	26	. 7.27	8.32
29	. 7.39	9.55	27	. 7.27	8.32
30	. 7.63	8.62	28	. 7.33	8.32
31	. 7.82	9.09	29	. 7.52	9.24
Sept. 1	. 7.45	8.62	30	. 7.45	8.78
2	. 7.39	9.09	31	. 7.45	9.70

Date.	Combined Car- bonic Acid.	Free Car- bonic Acid.
Nov. 1	7.39	8.70
2	7.27	8.70
3	7.33	8.47
4	7.39	8.47
5	7.52	8.05
6	7.39	7.73
7	7.39	9.16
8	7.52	7.55
9	7.39	8.47
10	7.39	8.47
11	7.39	8.01
12	7.33	8.01
13	7.39	8.01
14	7.39	8.24
15	7.33	8.01
16	7.33	8.49
17	7.33	8.93
18	7.33	8.93
19	7.57	9.39
20	7.33	9.86
21	7.33	9.39
22	7.33	8.93
23	7.33	8.93
24	7.33	9.39
25	7.33	9.24
26	7.27	9.93
27	7.27	9.47
28	7.33	10.16
29	7.39	8.32
30	7.33	8.78
Dec. 1	7.27	9.24
2	7.27	8.78
3	7.33	8.78
4	7.33	9.70
5	7.39	9.24
6	7.39	9.70
7	7.27	9.24
8	7.33	9.24
9	7.27	8.32
10	7.39	8.78
11	7.39	9.24
12	7.33	9.24
13	7.33	8.32
14	7.33	9.24
15	7.33	9.68
16	7.33	8.78
17	7.33	9.70
18	7.33	9.24
19	7.33	9.24
20	7.39	9.24
21	7.33	9.68
22	7.33	9.68
23	7.27	10.16
24	7.39	8.78
25	7.33	10.16
26	7.33	8.78
27	7.42	9.70
28	7.33	9.24
29	7.36	10.16

Date.	Combined Car- bonic Acid.	Free Car- bonic Acid.
Dec. 30	7.33	8.32
31	7.52	7.86
Jan. 1	7.33	8.78
2	7.27	9.70
3	7.27	9.24
4	7.33	9.70
5	7.42	8.32
6	7.27	8.78
7	7.33	9.24
8	7.27	9.24
9	7.27	8.78
10	7.33	9.24
11	7.33	8.09
12	7.33	8.09
13	7.33	8.78
14	7.33	8.78
15	7.33	8.78
16	7.21	9.24
17	7.27	8.32
18	7.52	9.24
19	7.52	10.16
20	7.42	8.78
21	7.33	10.16
22	7.33	8.32
23	7.39	8.32
24	7.26	8.78
25	7.39	7.85
26	7.33	6.93
27	7.33	7.85
28	7.36	7.85
29	7.33	8.78
30	7.33	8.78
31	7.27	8.78
Feb. 1	7.64	9.70
2	7.52	8.78
3	7.39	8.32
4	7.33	8.32
5	7.42	9.24
6	7.39	8.78
7	7.52	8.78
8	7.58	8.78
9	7.64	8.16
10	7.64	8.62
11	7.70	8.42
12	7.64	8.42
13	7.64	8.42
14	7.64	8.99
15	7.52	8.99
16	7.58	8.62
17	7.58	10.01
18	7.52	10.01
19	7.52	8.62
20	7.42	8.62
21	7.42	7.70
22	7.58	7.70
23	7.64	8.62
24	7.64	8.62
25	7.52	8.62
26	7.58	8.93

Date.	Combined Car- bonic Acid.	Free Car- bonic Acid.
Feb. 27	. 7.52	8.16
28	. 7.52	8.62
Mar. 1	. 7.52	9.08
2	. 7.58	8.16
3	. 7.70	8.16
4	. 7.36	7.70
5	. 7.52	8.16
6	. 7.52	8.62
7	. 7.64	8.62
8	. 7.52	8.62
9	. 7.33	8.16
10	. 7.39	7.55
11	. 7.33	8.47
12	. 7.36	8.01
13	. 7.27	8.47
14	. 7.27	8.47
15	. 7.33	8.01
16	. 7.42	8.47
17	. 7.33	8.47
18	. 7.51	8.01
19	. 7.47	8.47
20	. 7.44	8.47
21	. 7.44	8.01
22	. 7.39	7.47
23	. 7.39	7.47
24	. 7.33	7.47
25	. 7.39	8.47
26	. 7.33	8.23
27	. 7.44	8.47
28	. 7.39	8.47
29	. 7.33	8.01
30	. 7.33	8.47

Date.	Combined Car- bonic Acid.	Free Car- bonic Acid.
Mar. 31	. 7.27	8.47
April 1	. 7.27	8.01
2	. 7.76	9.39
3	. 7.27	8.47
4	. 7.33	9.87
5	. 7.33	8.47
6	. 7.58	8.47
7	. 7.39	8.47
8	. 7.44	8.47
9	. 7.33	8.47
10	. 7.33	8.93
11	. 7.39	8.01
12	. 7.39	8.01
13	. 7.33	8.47
14	. 7.27	8.47
15	. 7.39	8.01
16	. 7.76	8.78
17	. 7.51	8.32
18	. 7.76	8.78
19	. 7.58	8.32
20	. 7.44	8.78
21	. 7.39	8.32
22	. 7.39	9.24
23	. 7.76	8.98
24	. 7.64	9.24
25	. 7.33	8.78
26	. 7.39	8.32
27	. 7.51	8.78
28	. 7.51	8.78
29	. 7.58	8.78
30	. 7.58	8.78

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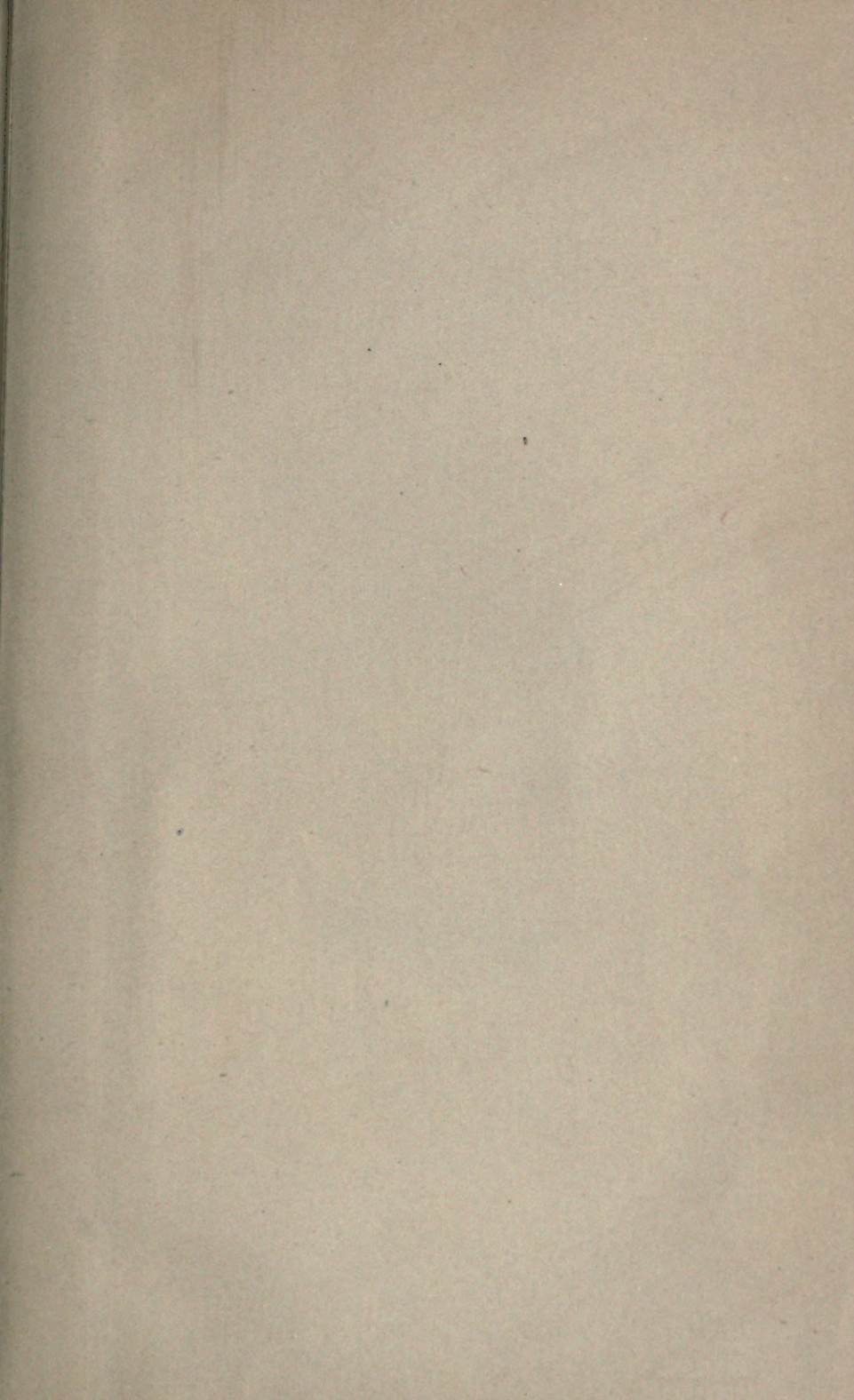
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